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DIELECTRIC MEASUREMENTS AT LOW TEMPERATURES  
OF CERTAIN SALTS OF THE IRON GROUP

by

ROBERT F. STURROCK B.Sc.

UNIVERSITY OF ALBERTA 1950

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DIELECTRIC MEASUREMENTS AT LOW TEMPERATURES  
OF CERTAIN SALTS OF THE IRON GROUP

A DISSERTATION  
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF MASTER OF SCIENCE

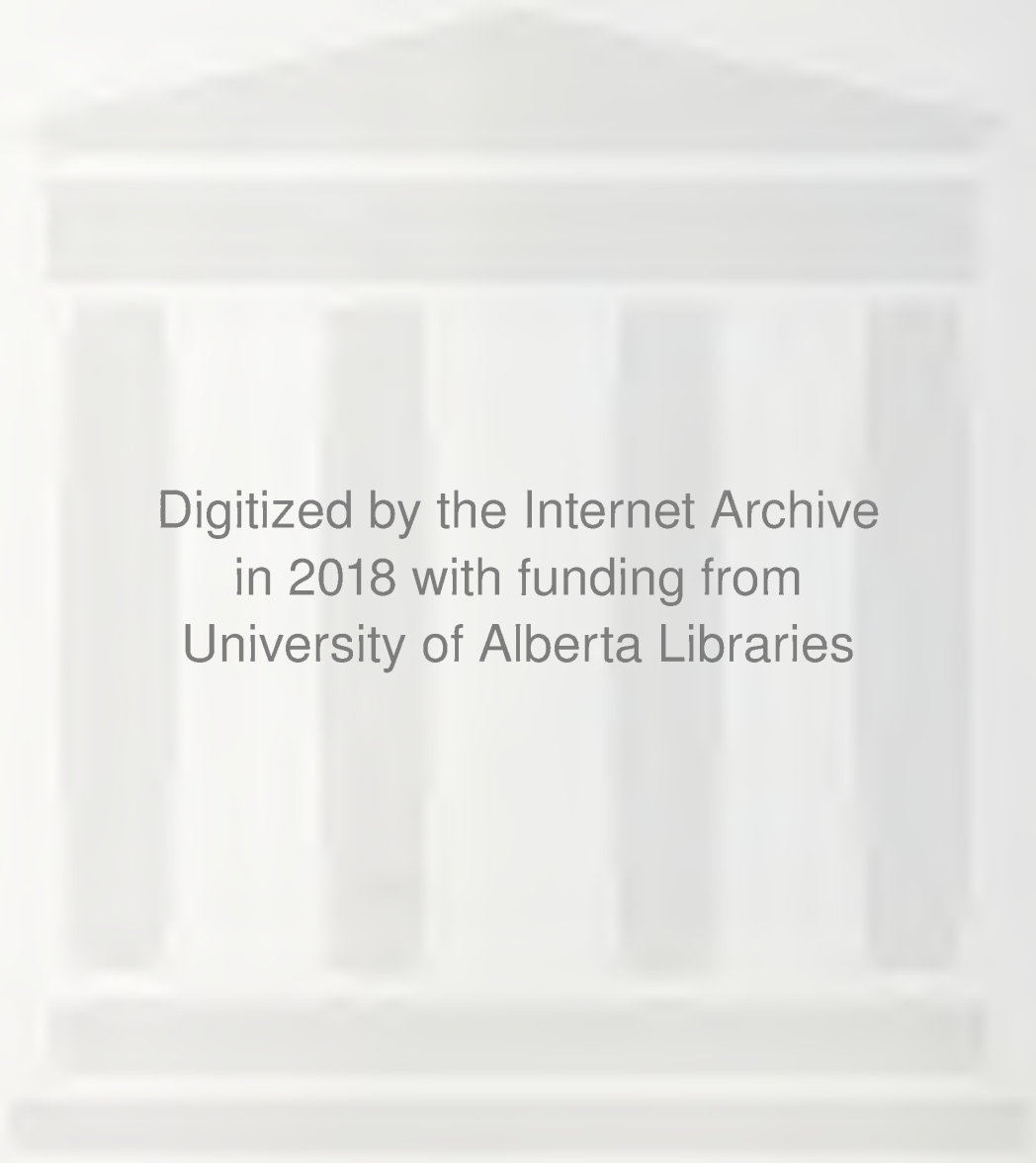
FACULTY OF ARTS AND SCIENCE

by

ROBERT FORBES STURROCK

EDMONTON, ALBERTA,

SEPTEMBER, 1950.



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Abstract

In order to provide further information on transitions of the second-order previously found in certain salts of the iron group, an investigation of their dielectric properties was undertaken. One salt, hydrated chromium sulphate, showed a dielectric anomaly corresponding to the transition. Considering also the evidence of the entropy change, it is suggested that this is due to the freeing at the transition point of two molecules of water per molecule of the salt. The nitrates which were investigated did not show a dielectric anomaly, and it is believed that the transitions in these cases are due to rotations of the nitrate radicals.

CHAPTER II

The first part of the book is devoted to a general introduction to the subject of the history of the English language. It is divided into three sections: the first section deals with the prehistoric period, the second with the Saxon period, and the third with the Norman period. The second part of the book is devoted to a detailed account of the history of the English language from the Saxon period to the present time. It is divided into two sections: the first section deals with the Saxon period, and the second with the Norman period. The third part of the book is devoted to a detailed account of the history of the English language from the Norman period to the present time. It is divided into two sections: the first section deals with the Norman period, and the second with the modern period.

# Introduction.

## (a) Second-Order Transition.

A transition of the second order may be defined (Zemansky<sup>1</sup>, Epstein<sup>2</sup>) as a phase change which takes place at constant temperature and pressure without a discontinuous change in entropy or volume. Such changes have also been termed co-operative changes and  $\lambda$  point transitions, and have been discussed as such by Fowler (3). The first derivatives of the Gibbs function,  $Z = U + PV - TS$ , are continuous across the boundary of the transition but the second derivatives may be discontinuous. In the latter case the discontinuities at the boundary are expressed by Ehrenfest's equations,

$$\left(\frac{dP}{dT}\right)_{T_0} = \frac{\Delta C_p}{TV\Delta\alpha} \quad (1)$$

$$\left(\frac{dP}{dT}\right)_{T_0} = \frac{\Delta\alpha}{\Delta K} \quad (2)$$

which may be combined to give,

$$\Delta C_p = TV \left(\frac{\Delta\alpha}{\Delta K}\right)^2 \quad (3)$$

where  $T_0$  is the transition temperature,  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$  is the volume expansion coefficient, and  $K = \frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$  is the compressibility.

In any case transitions of the second order are easily recognized by the characteristic shape of the specific heat - temperature curve, which shows a very sharp maximum at the transition temperature. There may be a discontinuous decrease in the specific heat at  $T_0$ , in agreement with equation (3). However, in many cases the discontinuity is replaced by a very sharp negative slope extending over a range of two or three degrees. Such transitions are clearly due to a change in the arrangement or orientation of the molecules, without appreciable change in volume. The change actually takes



place continuously over a certain range of temperature, without the appearance of a mixed phase, and is complete or nearly complete at the temperature  $T_0$  of the specific heat maximum. There is, however, energy required to produce the change, and there is a large increase in entropy which is statistically related to an increase in the degree of disorder.

A typical example is the order-disorder transition in  $\beta$ -brass, (Burton, Grayson-Smith and Wilhelm<sup>4</sup>). This material has the approximate formula CuZn, and crystallizes in what may be considered as two interpenetrating simple cubic lattices. At low temperatures one simple cubic lattice is occupied by Cu atoms and the other by Zn atoms, giving an ordered state. Above the transition temperature the points on the lattice are occupied indiscriminately by Cu and Zn atoms, and the substance is said to be in the disordered state. It follows from Boltzmann's law,

$$S = k \ln W, \quad (4)$$

where  $W$  is the number of configurations of a body, that the total entropy change due to an order-disorder transition in a binary alloy is

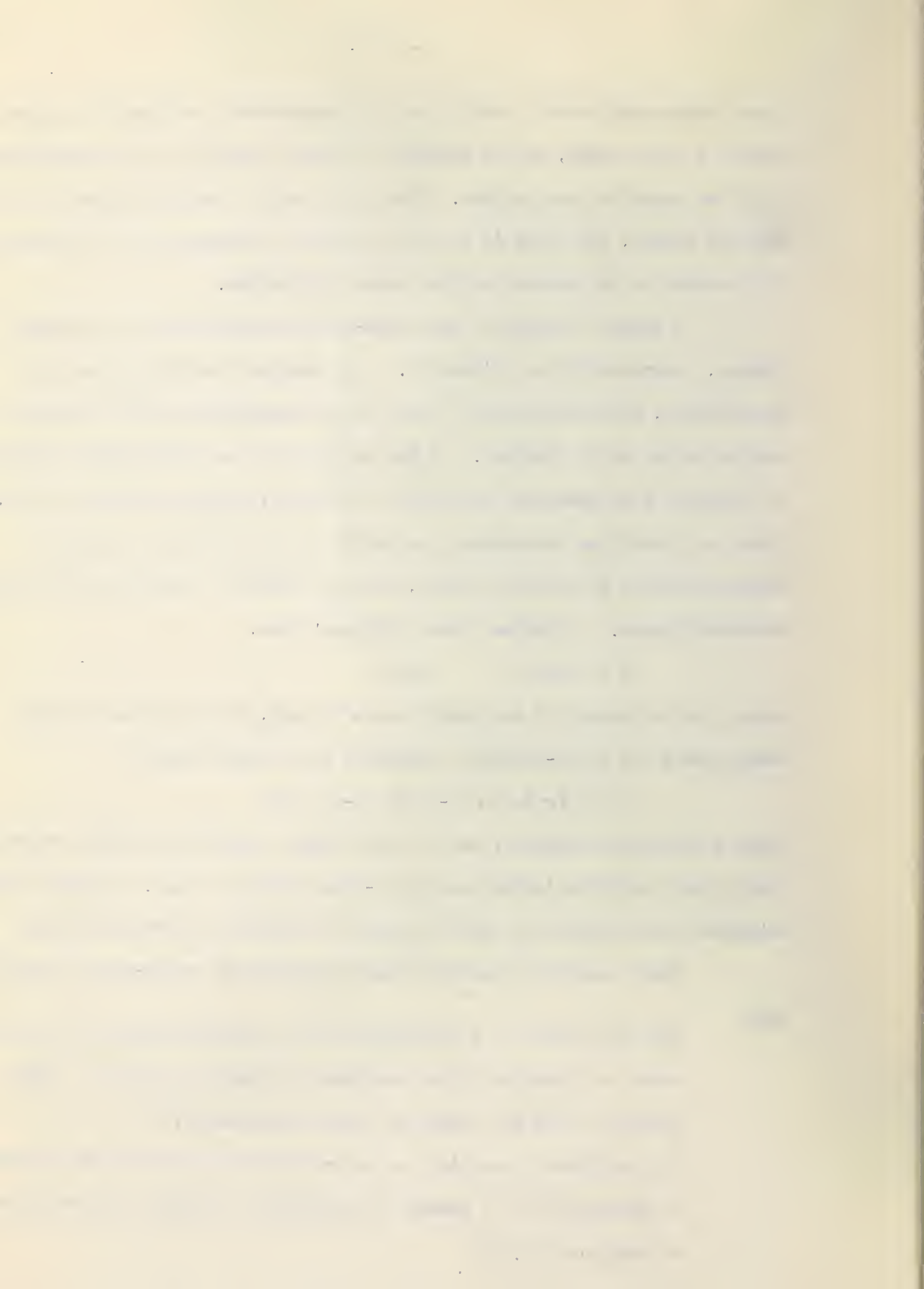
$$S = R \{ r \ln r + (1-r) \ln (1-r) \} \quad (5)$$

where  $R$  is the gas constant, and  $r$  is the atomic fraction of either component. This is well verified in the case of  $\beta$ -brass, where  $r = 1/2$ . Further, the existence and structure of the two states is confirmed by X-ray analysis.

Other examples which have been recognized as second-order transitions are:

The Curie point of a ferromagnetic or anti-ferromagnetic material where the electron spins pass from an ordered, parallel or anti-parallel state to a state of random orientation.<sup>(5)</sup>

The analogous transition in ferro-electric barium titanate which is accompanied by a change in crystalline structure from tetragonal to pseudo-cubic.<sup>(6)</sup>



The transitions in  $\text{NH}_4\text{Cl}$  and in some of the hydrogen halides, which are ascribed to the onset of free rotation of the  $\text{NH}_4\text{HCl}$ , etc., groups within the crystal<sup>(3)</sup>.

(b) Salts of the Iron Group.

Vasileff (7) has measured the specific heats of several salts of the iron group metals down to the temperature of liquid air. Specific heat anomalies were found for the hydrated salts with maxima at the following temperatures:

$\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	158°K
$\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	158°K
$\text{Ni}(\text{NO}_2)_2 \cdot 6 \text{H}_2\text{O}$	150°K
$\text{Cr}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$	195°K

The anhydrous form of chromium sulphate,  $\text{Cr}_2(\text{SO}_4)_3$ , was also measured, but no specific heat anomaly was found. All the anomalies had the characteristic shape of second-order transitions, indicating some type of co-operative change within the crystal.

Since the transition metals are all paramagnetic, it was at first thought likely that the explanation might lie in a paramagnetic transition with a definite Curie temperature. Measurements of the magnetic susceptibilities of the salts in question were carried out by Johnson<sup>and Grayson-Smith</sup> (8) at the University of Toronto. No anomalies were found in the magnetic properties of any of the materials, and hence this explanation was found unsatisfactory.

The most likely remaining explanation was that the anomalies were due to the onset of rotation in either the water groups or the nitrate or sulphate radicals. In the case of chromium sulphate, rotation of one or more water groups appeared likely in view of the absence of a specific heat anomaly in the anhydrous form. Because of the large dipole moment of the



water molecule, the onset of rotation should produce a marked effect on the dielectric constant. Accordingly the present investigation was undertaken to measure the dielectric properties of this group of salts over the region of the specific heat anomalies.



## Experimental Method

### A. General.

The dielectric properties of the substances under investigation were determined by the following method. A dielectric cell, consisting of two concentric brass cylinders, was filled with a known mass of the material in a finely powdered form. The cell was then suspended over evaporating liquid air in a vacuum flask, and allowed to cool slowly. During the cooling process the capacitance of the cell was measured by means of a modified Wien bridge operating at a frequency of 10,000 cycles per second. The temperature was determined by means of copper-constantan thermocouples fixed to the inner and outer cylinders of the cell. Readings of capacitance and temperature were taken down to a temperature of about 100°K. The cell was then allowed to warm up slowly and a second set of readings taken for a rising temperature.

The dielectric constant of the mixture of salt and air in the cell was computed by taking the ratio of the measured capacitance of the cell to the calculated capacitance of the empty cell.

The total polarizability of the salt was then computed from the formula

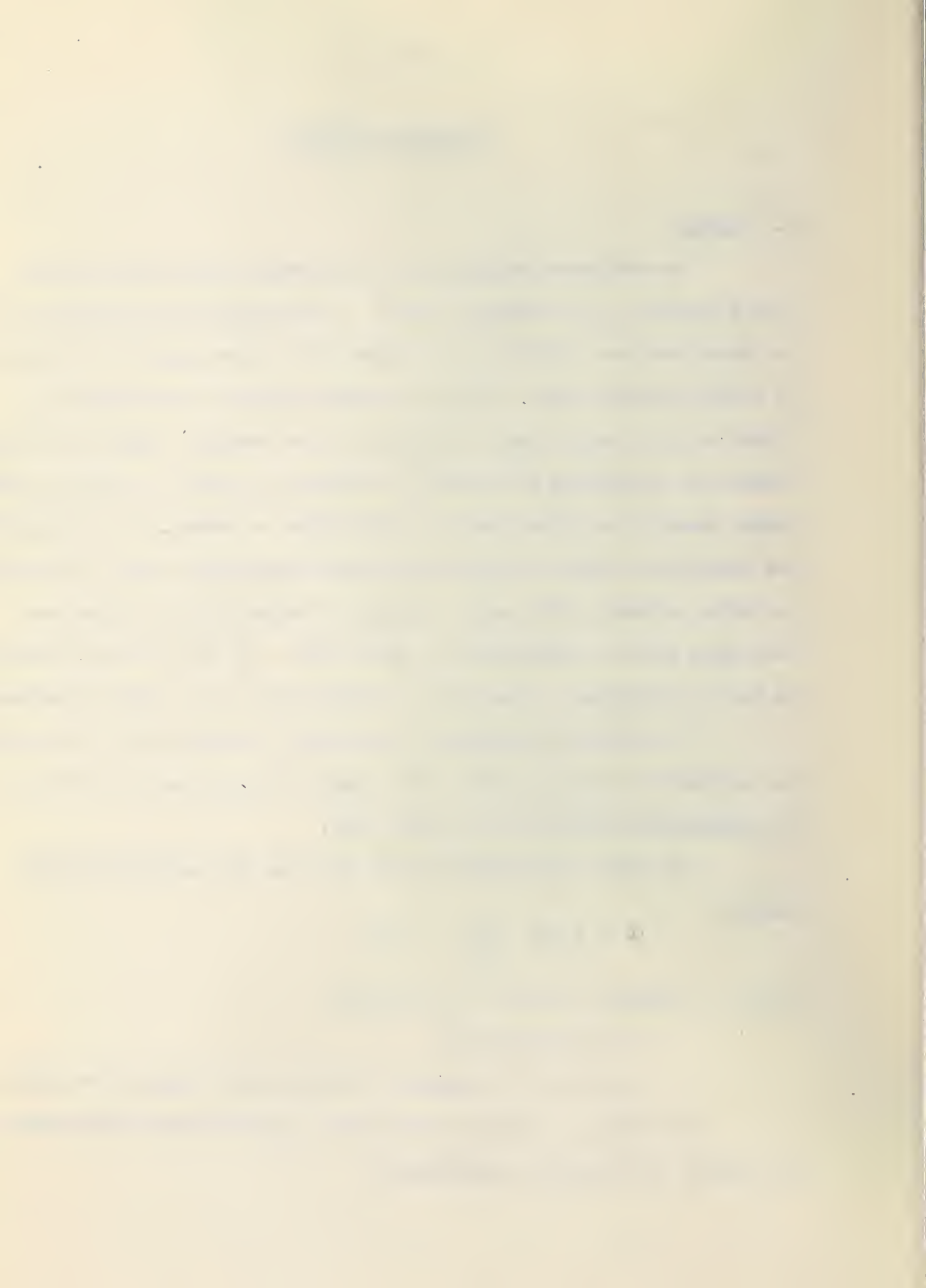
$$\alpha = \frac{K - 1}{K + 2} \frac{3}{4\pi n_1} \quad (6)$$

where K    dielectric constant of the mixture

$\alpha$  = polarizability

$n_1$  = number of molecules of salt per unit volume of the cell.

The values of polarizability versus temperature were then plotted for each of the substances investigated.



## B. Dielectric Cell.

The cell used is shown in Figure I. It consisted of two co-axial brass cylinders A,C, held in place by lucite plugs D,E. The space between the cylinders was packed with the salt whose dielectric properties were being measured. A portion of both cylinders was threaded as shown in the diagram to facilitate easy dismantling of the cell. To provide an air-tight seal at the ends of the cell a small amount of "liquid solder" was spread on the threaded portion of the lucite plugs before final closing off of the cell after filling. This material was found to harden quickly and to resist cracking at low temperature. Two small brass bolts J were used to mount the cell in position on the cover assembly.

The mean dimensions of the cell were as follows:

Inner diameter of outer cylinder = 4.242 cm.

Outer diameter of inner cylinder = 3.812 cm.

Height of inner cylinder = 8.781 cm.

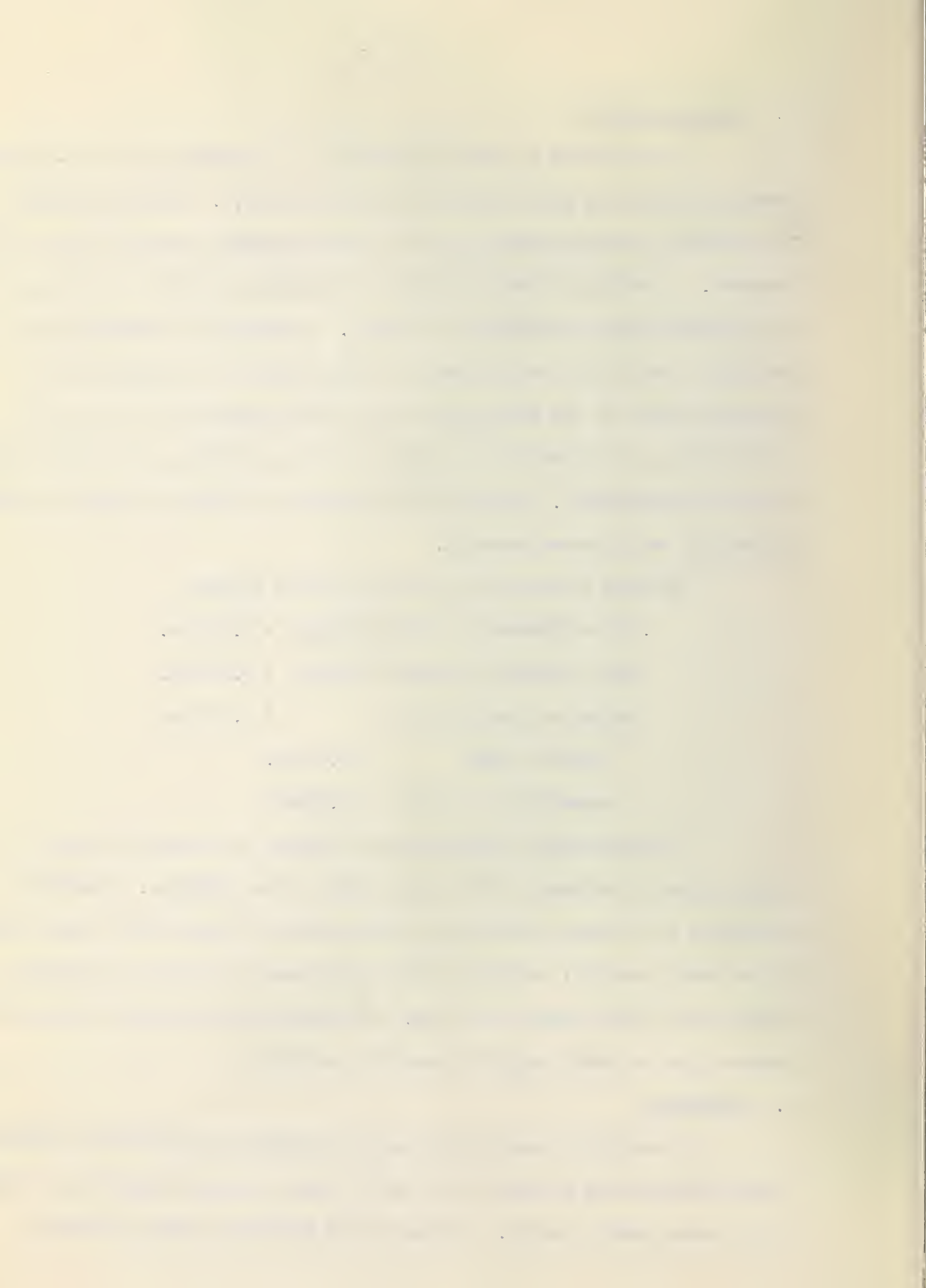
Volume of cell = 23.88 cc.

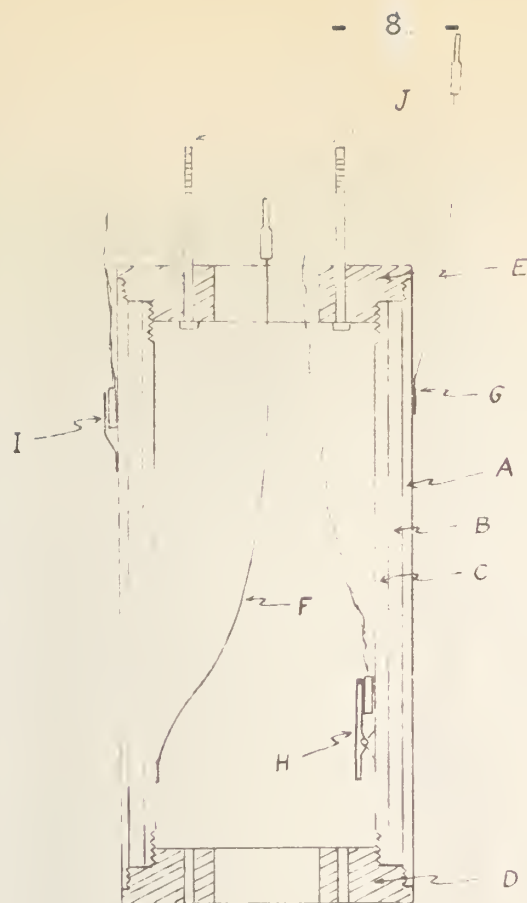
Capacitance in vacuum = 45.65  $\mu$ uf.

The thermocouple junctions were fastened to the cell by means of spring clips I,H soldered to the brass walls of the cylinders. Electrical connection to the outer wall of the cell was made by means of the brass tubing in the cover assembly, while the leads to the inner wall and to the thermocouples were taken through this tube. All electrical connections were of the plug-in type to permit complete removal of the cell.

## C. Cryostat.

The method of controlling the temperature is illustrated in Figure 2, A vacuum flask about 12 inches high and  $2\frac{3}{4}$  inches internal diameter was fitted with a brass cover as shown. A piece of  $\frac{1}{2}$  inch brass tubing C running





- A - Outer brass cylinder
- B - Dielectric material
- C - Inner brass cylinder
- D - Lower lucite cap
- E - Upper lucite cap
- F - Spring wire connection to inner cylinder
- G - Connection to outer cylinder
- H - Spring clip for inner thermocouple junction
- I - Spring clip for outer thermocouple junction
- J - Brass stud bolts

Figure 1      DIELECTRIC CELL

Scale    1 inch = 3 cm



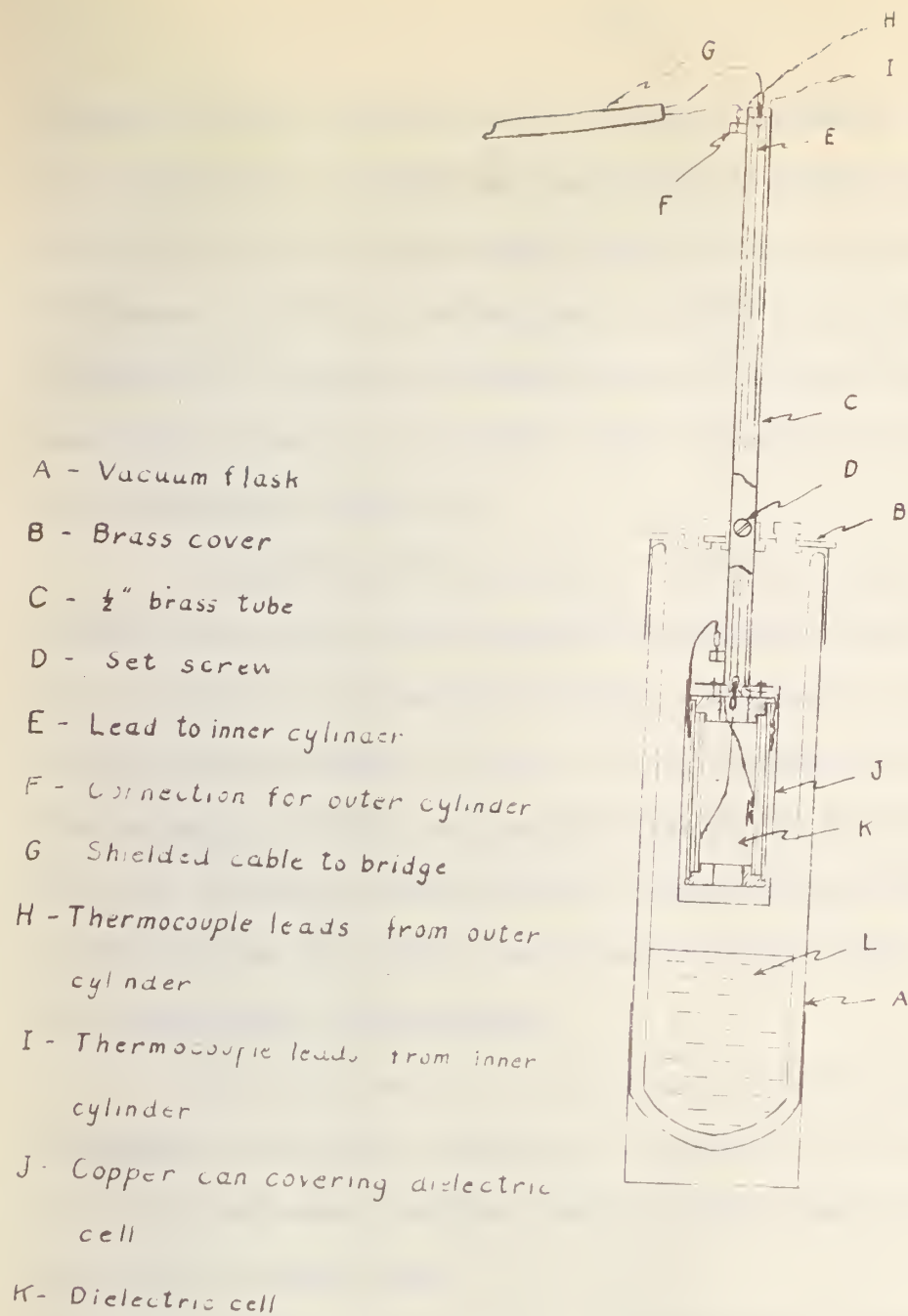


Figure 2

COOLING ASSEMBLY

Scale  $\frac{1}{3}$



through the cover served both as a means of raising or lowering the cell in the flask and as a conduit for the various electrical leads to the cell. The cell could be set at any desired level by means of the set screw D and by this means the rate of cooling could be readily controlled. To prevent the possibility of liquid air seeping into the dielectric cell a copper can J was placed around it. This also helped to make the temperature more uniform over the height of the cell.

During the initial stages of cooling the cell was kept in the upper portion of the flask, and as cooling progressed, it was lowered gradually. With the covering can partly immersed in liquid air a temperature of about  $100^{\circ}\text{K}$  could be reached. To take a set of readings for increasing temperature the foregoing procedure was merely reversed, the cell being raised gradually. The time to bring the cell from room temperature to  $100^{\circ}\text{K}$  was normally about eight hours and the warming period was about six hours.

#### D. Measurement of Temperature.

The temperature of the cell was measured by means of a copper-constantan thermocouple fastened by a spring clip to the inner wall of the cell. The reference junctions were soldered to small brass plates which were kept in crushed ice.

Readings of the e.m.f. of both thermocouples were made with a Leeds and Northrup Type K potentiometer. In order to increase the sensitivity an external galvanometer was used in place of that in the potentiometer assembly. With this the e.m.f. could be read fairly easily to 0.1 millivolts, corresponding to about 0.3 degrees over the range of temperatures measured. Since setting of the capacitance bridge could be obtained quickly, the procedure in taking observations was to set the potentiometer exactly on a marked division and make a capacitance setting as soon as the temperature of the cell reached this



point, as indicated by zero deflection of the galvanometer. The e.m.f. of the other thermocouple could then be read by throwing the switch connecting it into the potentiometer circuit and noting the deflection of the galvanometer needle from zero. For the normal rate of cooling the differences in temperature between the inner and outer thermocouples did not exceed three or four degrees.

The temperature of the material in the cell was taken to be that of the inner thermocouple. This was done since there was a suspicion that the outer thermocouple was affected slightly by its proximity to the outer jacket, and because the readings of the inner thermocouple were much more stable. The error involved is not believed to exceed one degree and changes of temperature are still accurate within about 0.3 degrees.

The thermocouples were calibrated at the ice point, the dry-ice point, and the boiling point of pure liquid oxygen. The differences  $\Delta t$  were taken between these temperatures and those given for the observed e.m.f.'s in the Leeds and Northrup conversion table for copper-constantan (38 calibration). It was assumed that  $\Delta t$  would be of the form,

$$\Delta t = a + bt^1 + ct^{1^2}$$

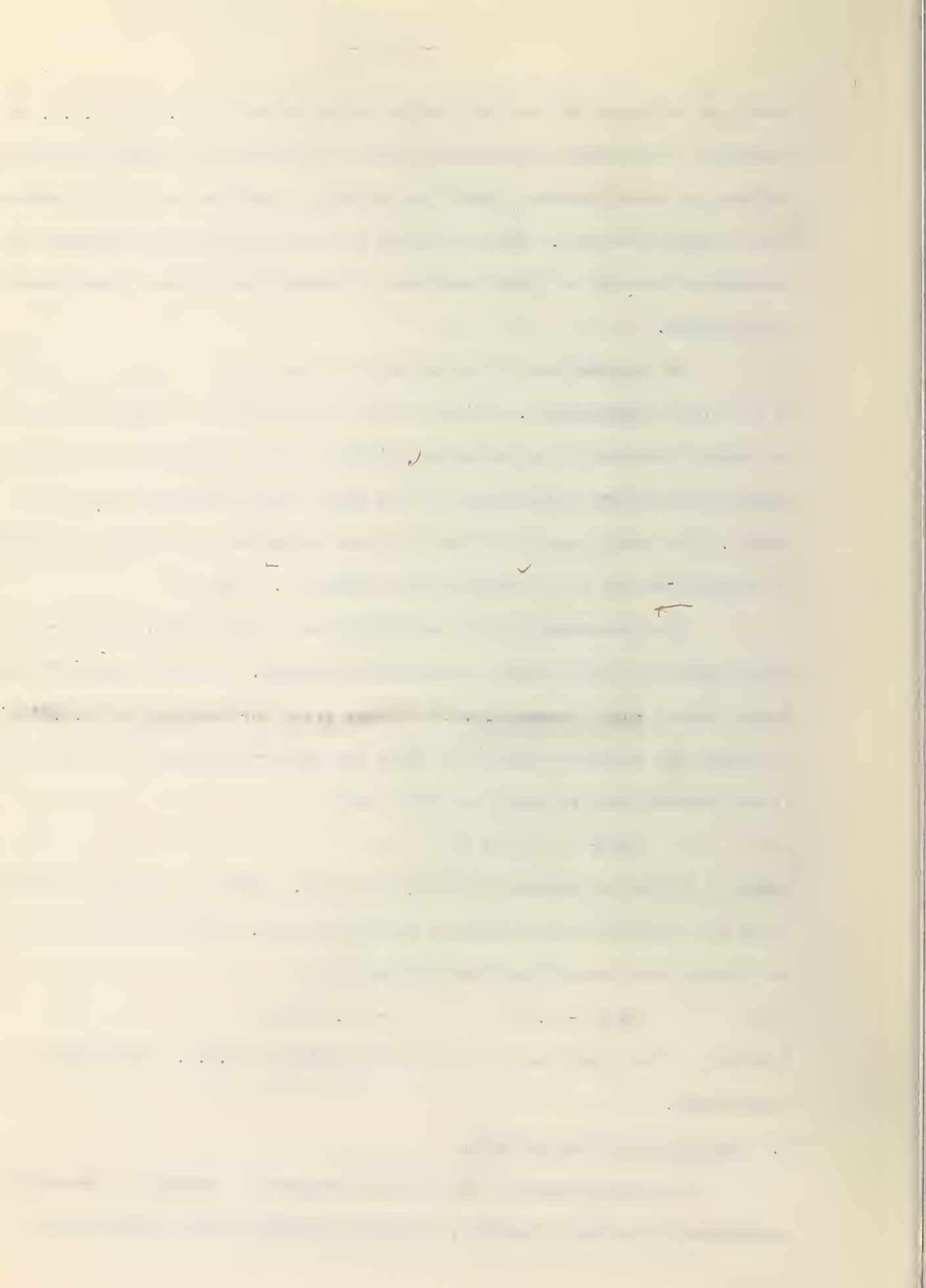
where  $t^1$  is the temperature given by the table. Since the reference junction is at the ice point the constant  $a$  is clearly zero. The constants  $b$  and  $c$  were found from the calibration readings to be

$$b = -0.0025 \qquad c = 0.000205$$

A table was then constructed to convert readings of e.m.f. into Kelvin temperature.

#### E. Measurement of Capacitance.

The capacitance of the cell was measured by means of a specially constructed Wien bridge circuit, with the positions of the detector and



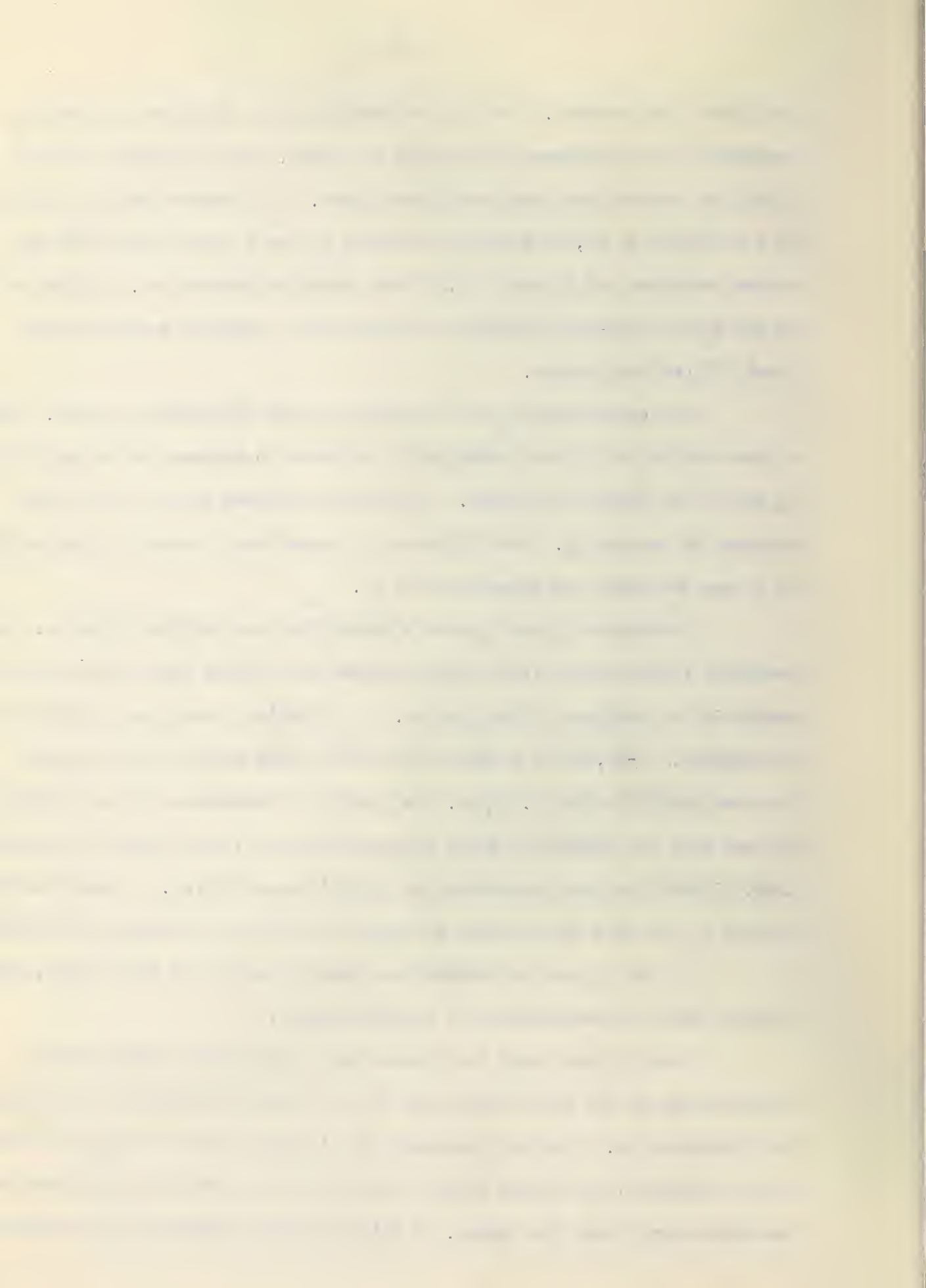
oscillator interchanged. The basic circuit is shown in Figure 4, where  $C_x$  represents the capacitance of the cell and leads. The oscillator used was a Hewlett Packard Model 200B audio oscillator. All measurements were taken at a frequency of 10,000 cycles per second.  $R_1$  and  $R_2$  were matched 600 ohm carbon resistors and  $R_3$  was a 10,000 ohm decade resistance box. Condensers  $C_1$  and  $C_2$  were two-gang variable condensers with a maximum capacitance of about 250  $\mu\text{pf}$  per section.

The capacitance  $C_x$  was determined by the substitution method. For a given setting of  $C_1$  the setting of  $C_2$  required to balance the bridge with  $C_x$  out of the circuit was noted.  $C_x$  was then replaced and the bridge re-balanced by varying  $C_2$ . The difference in capacitance between the two settings of  $C_2$  was therefore the capacitance of  $C_x$ .

Condensers  $C_1$  and  $C_2$  were obtained from war surplus equipment. An excellent feature was a 1:100 ratio between the control knob and the rotor shaft with no backlash in the gearing. By attaching a scale and pointer to the control, 1/10,000 of a turn of the rotor shaft could easily be read. This was equal to about 0.03  $\mu\text{pf}$ . To provide an adequate range of capacitance for use with the dielectric cell, both sections of  $C_1$  were connected in parallel, giving a maximum capacitance of slightly over 500  $\mu\text{pf}$ . A single section only of  $C_2$  was used as this made it easier to read small changes in capacitance.

$C_1$  and  $C_2$  were calibrated on a General Radio Type 650A bridge, using a Dumont Type 168 oscilloscope as a null detector.

Later it was found that there was a considerable change in the balance point of the Wien bridge when the two leads from the audio oscillator were interchanged. This was apparently due to some type of leakage with the audio oscillator, but it was thought advisable to recheck the capacitance of the condensers within the bridge. A third variable condenser  $C_3$  was calibrated



on the General Radio bridge, and substituted for  $C_x$  in the Wien bridge circuit. The three condensers were then intercompared.

The observational error in calibrating the condensers was about 0.1  $\mu\text{pf}$ , but does not include the error in the bridge itself which is probably somewhat greater than this. However the error in the bridge would cancel out in the final calculation of the dielectric constant, assuming that it is a constant percentage error. Since the observational error in the calibration was greater than the accuracy to which readings could be taken on the Wien bridge, the values were smoothed by plotting the capacitance  $C_x$  against the reading of  $C_2$ .

The salts to be measured were all found to be slightly conducting down to about  $-50^\circ\text{C}$ , and the effective resistance of the cell was found to depend on frequency. Therefore the bridge could not be properly balanced when harmonics of the oscillator frequency were present. To eliminate this the output from the detector terminals was fed through a composite low-pass filter designed to attenuate all harmonics of the supply frequency. The voltage was then amplified, using the amplifier circuit in a 5 inch oscilloscope. The output from the latter was fed into a 3 inch R.C.A. oscilloscope to indicate the null point of the bridge balance. With this arrangement the oscilloscope trace showed a perfectly flat minimum even with all controls turned to a maximum gain. Another stage of amplification could have been added if greater sensitivity had been desired.

The low-pass filter circuit is shown in Figure 5 and the design data are given in Table 1. It consisted of a constant-K section designed to pass all frequencies up to 11,000 cycles per second, an infinite attenuation section with a frequency of 12,200 cycles for maximum attenuation, and an m-derived section with  $m = 0.6$ . The design was based on the values of inductances



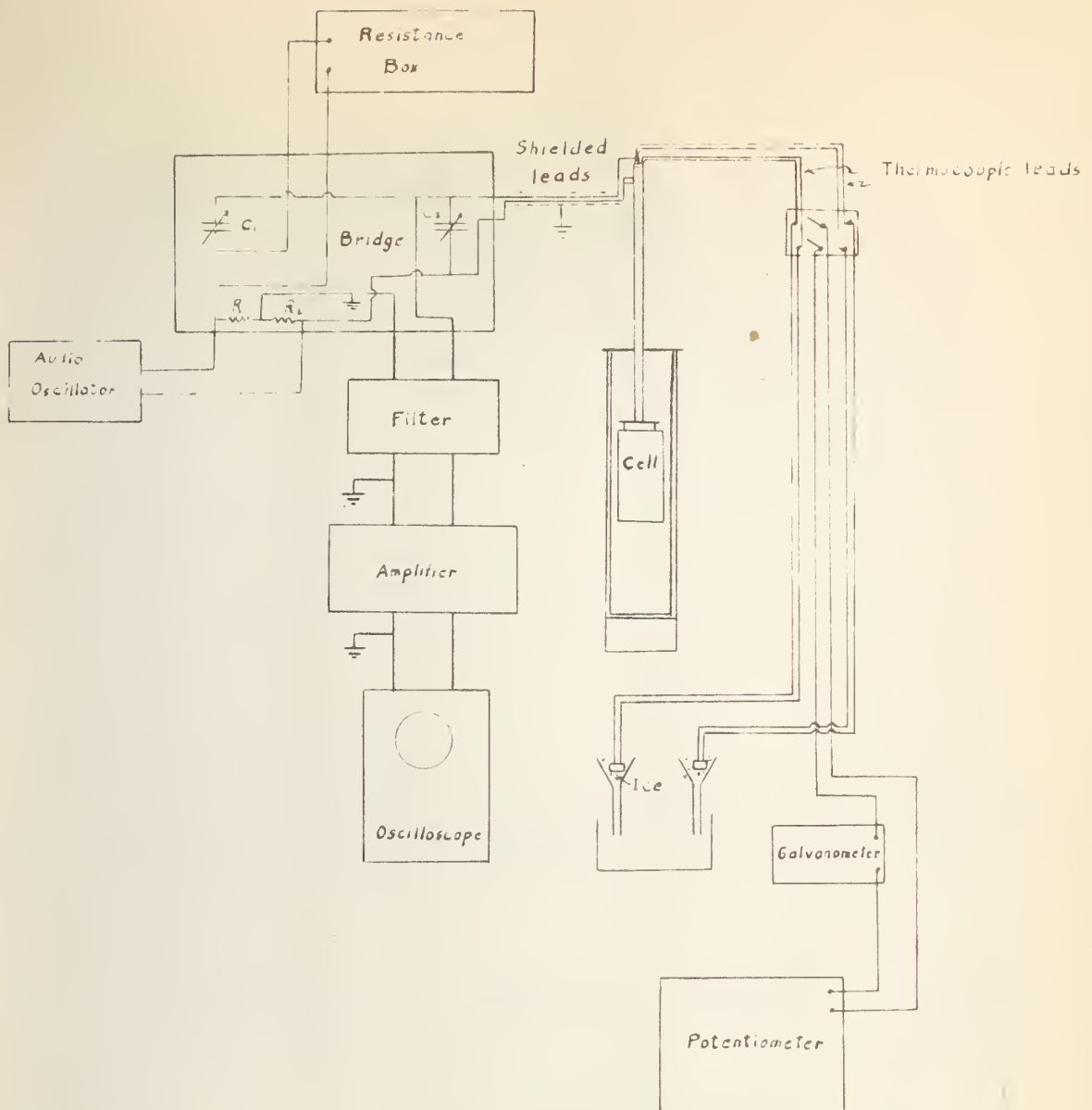


Figure 3 SCHEMATIC ARRANGEMENT OF APPARATUS



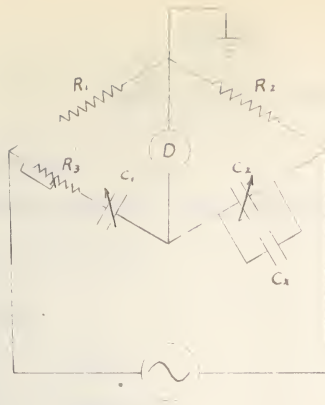


Figure 4 BRIDGE CIRCUIT FOR CAPACITY MEASUREMENT

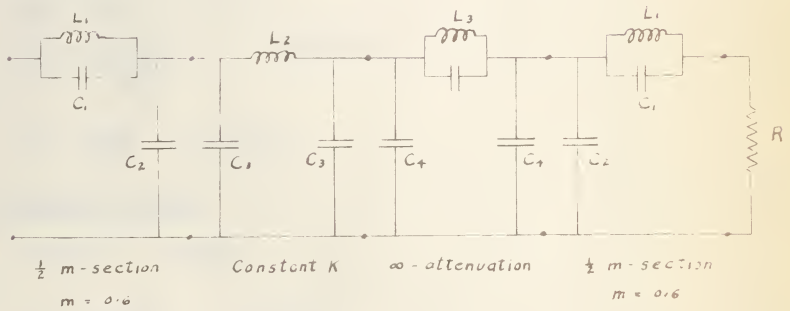


Figure 5 LOW-PASS FILTER CIRCUIT

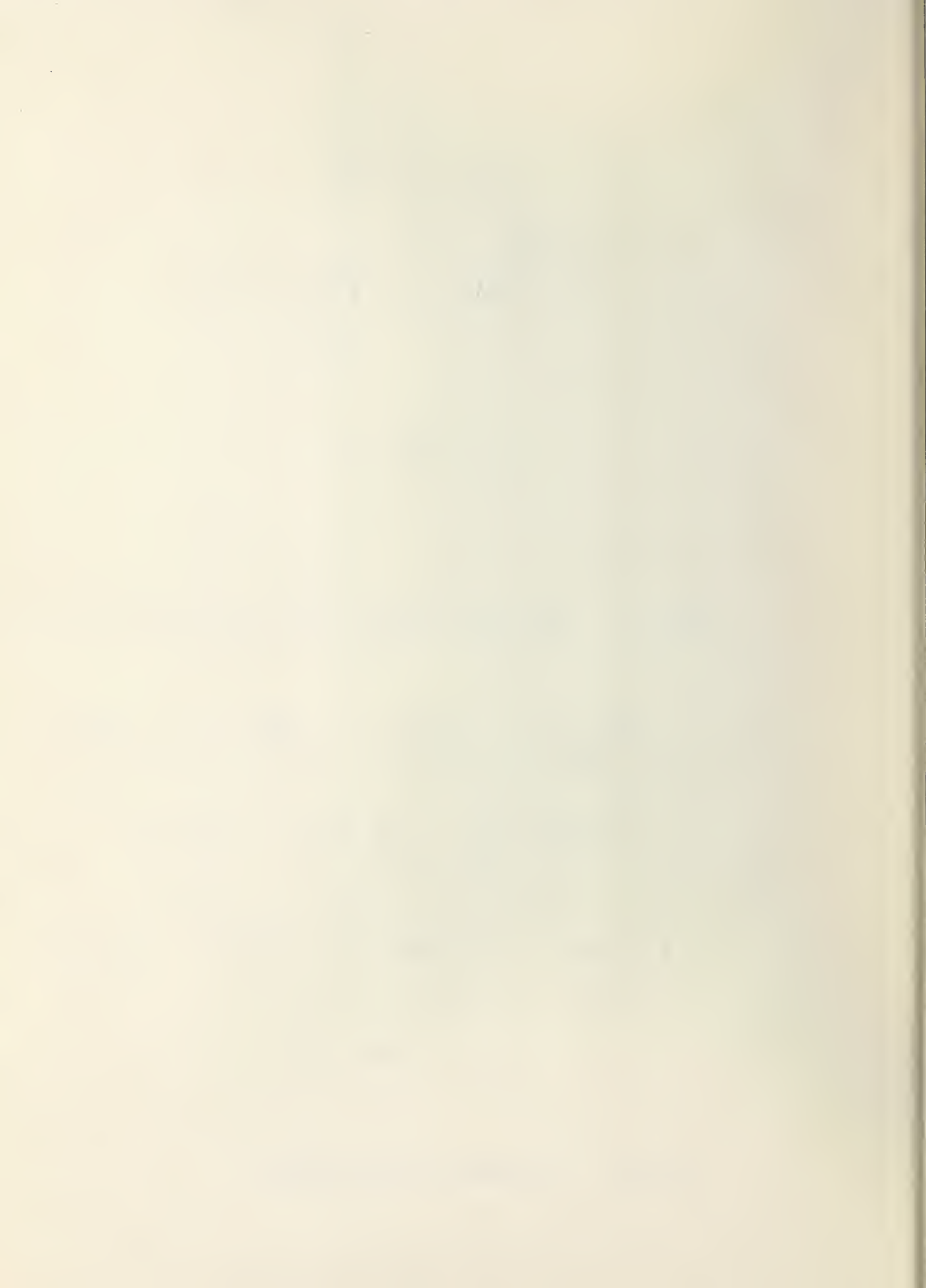


Table I.

Design Data of Low-Pass Filter.

Constant-K Section.

$f_c$  = cut-off frequency = 10,000 cycles per second.

$$L = \frac{R}{\pi f_c} = 25 \text{ mh} = L_2$$

$$R = 863 \text{ ohms}$$

$$C = \frac{1}{\pi R f_c} = 0.0336 \text{ } \mu\text{f}$$

$$C_3 = \frac{C}{2} = 0.0168 \text{ } \mu\text{f}$$

Infinite Attenuation Section.

$f_{\infty}$  = frequency of maximum attenuation = 12,200 cycles per second.

$$m_{\infty} = 1 - \frac{f_c^2}{f_{\infty}^2} = 0.415$$

$$L_3 = m_{\infty} L = 10.35 \text{ mh}$$

$$C_5 = \frac{1 - m_{\infty}^2}{4m_{\infty}} C = 0.0166 \text{ } \mu\text{f}$$

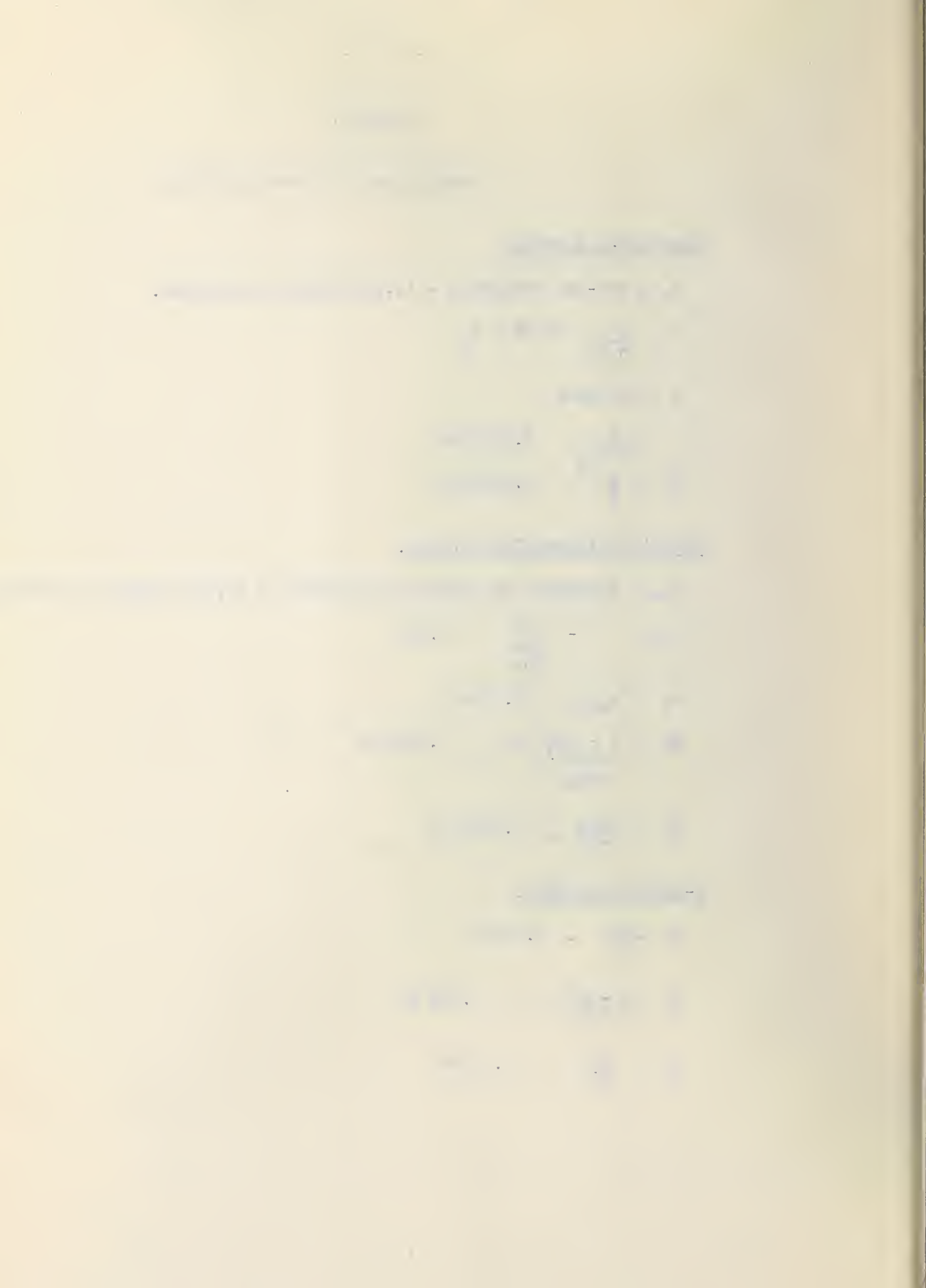
$$C_4 = \frac{m_{\infty} C}{2} = 0.0007 \text{ } \mu\text{f}$$

m-derived Section.

$$L_1 = \frac{mL}{2} = 7.5 \text{ mh}$$

$$C_1 = \frac{1 - m^2}{2m} C = 0.018 \text{ } \mu\text{f}$$

$$C_2 = \frac{mC}{2} = 0.01 \text{ } \mu\text{f}$$



available, which were all of the toroidal type. Exact measurements of the amount of attenuation for different frequencies were not made, but the first harmonic of 10,000 cycles appeared to be attenuated by a factor of about 60.

#### F. Measurement of Resistance.

The resistance balance was obtained by means of a 10,000 ohm resistance box  $R_3$  in series with  $C_1$  as shown in Figure 5. Analysis of the balance conditions of the circuit shows that at balance

$$R_3 = X_c^2 (G_x + G^1) \quad (7)$$

where  $X_c$  is the reactance of  $C_1$ ,  $G_x$  is the conductance of the cell, and  $G^1$  is the conductance of the leads and standard condenser. In the tabulation of measurements it was not considered necessary to convert the readings of  $R_3$  into the actual conductance of the cell since this was only of qualitative interest.

#### G. Materials Investigated and Their Preparation.

The salts measured and their maximum impurities as specified by the manufacturer are listed in Table II. All the salts were obtained from British Drug Houses (Canada) Ltd.

The sample of anhydrous chromium sulphate was prepared by heating the hydrate at about 400°C until the weight was constant. The mean weight loss of three samples was 41.9%  $\pm$  0.2%. This corresponds to the removal of 16.7 H<sub>2</sub>O per molecule and indicates that some drying of the salt had occurred. Mellor (9) lists several values for the water of hydration as found by different observers. The fractional value obtained is probably due to the presence of one or more of these forms. The molecular weight of the hydrate was taken to be 692.4 on the basis of the dehydration data.

<sup>and Grayson-Smith</sup>  
Johnson<sub>^</sub>(8) had found that all of the salts were deliquescent, hence sealing within the dielectric cell was performed as quickly as possible.

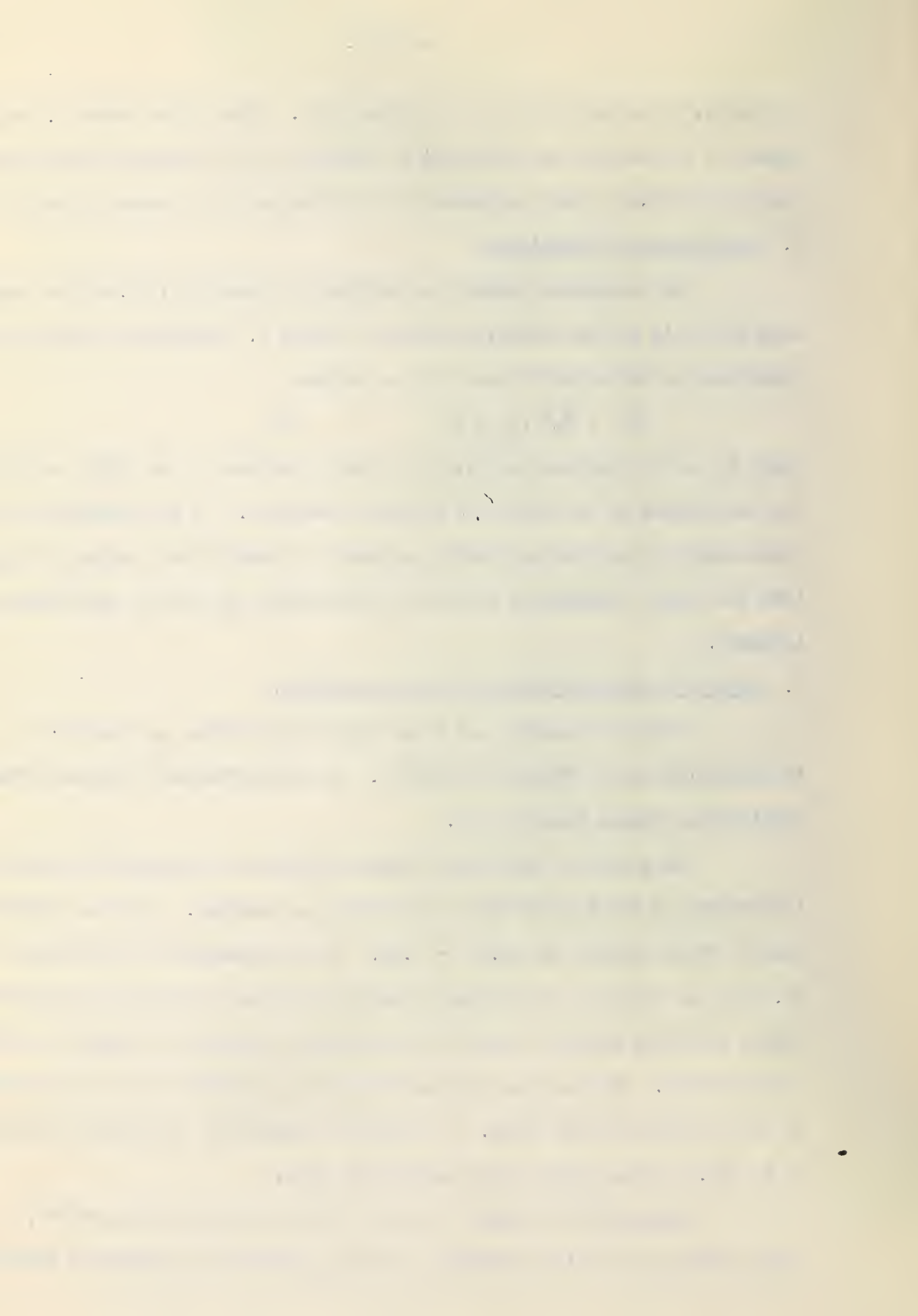


Table II.

Specifications of Salts Measured.

Chromium sulphate	$\text{Cr}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$	$M = 692.4^x$
Chloride (Cl)	0.0003%	
Iron (Fe)	0.01%	
Alkalis	0.5%	
Anhydrous chromium sulphate	$\text{Cr}_2(\text{SO}_4)_3$	$M = 392.20$
Chromium nitrate	$\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$	$M = 400.18$
Chloride (Cl)	0.003%	
Sulphate ( $\text{SO}_4$ )	0.01%	
Iron (Fe)	0.01%	
Alkalis	0.5%	
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$	$M = 290.80$
Chloride (Cl)	0.002%	
Sulphate ( $\text{SO}_4$ )	0.01%	
Cobalt (Co)	0.0005%	
Iron (Fe)	0.0001%	
Zinc (Zn)	0.0025%	
Alkalis and alkaline earths (Na)	0.03%	

<sup>x</sup> Calculated value from loss of weight in dehydration.



In the case of the nitrates it was found necessary to dry the samples for two or three days in a sulphuric acid dessicator before using them in the cell, since there was visible excess moisture.

#### H. Calculation of the Polarizability.

The total polarizability of a substance is given in terms of its dielectric constant by the Clausius-Mosotti equation,

$$\frac{K - 1}{K + 2} = \frac{4 \pi n}{3} \alpha \quad (8)$$

where K is the dielectric constant,  $\alpha$  is the polarizability and n is the number of molecules per cc.

In the case of a mixture of two substances we may write (10)

$$\frac{K - 1}{K + 2} = \frac{4 \pi}{3} n_1 \alpha_1 + \frac{4 \pi}{3} n_2 \alpha_2 \quad (9)$$

where K is the dielectric constant of the mixture,  $\alpha_1$  and  $\alpha_2$  are the polarizabilities of the components in the mixture, and  $n_1$  and  $n_2$  are the number of molecules per cc. of each component. The derivation may be shown to be true for spherical or cubical particles (11) and it is assumed to be true for the substances investigated.

Since the mixture in this case consisted of air and solid it is evident from equation (9) that the polarizability is given very closely by

$$\frac{K - 1}{K + 2} = \frac{4 \pi}{3} n_1 \alpha_1 \quad (10)$$

since  $\alpha$  for air is very nearly zero.

The results were plotted in terms of the polarizability rather than the dielectric constant since determination of the latter requires a knowledge of the density of the substance used. Densities of these salts as measured by different observers have been given by Mellor (9), but the values listed are quite inconsistent with each other. The densities of the samples used in this investigation were measured by means of a pycnometer, and by



other methods, <sup>but</sup> are still somewhat uncertain. The results are shown in Table III.

$n_1$  in equation (10) may be found by the equation

$$n_1 = \frac{mN}{MV} \quad (11)$$

where  $m$  is the mass of material in grams,  $N$  is Avogadro's number,  $M$  is the molecular weight, and  $V$  is the volume of the cell. Therefore it is unnecessary to know the density accurately.

TABLE III

Salt	<u>Specific Gravity</u>			
	Experimental value	Values from literature		
$\text{Cr}_2 (\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	1.86	1.696	1.840	1.867
$\text{Cr}_2 (\text{NO}_4)_3$	3.04, 3.18	2.221	2.743	3.012, 3.712
$\text{Cr} (\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.81			
$\text{N}_1 (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.02	1.993	2.065	2.037, 2.002



Chromium Sulphate Hydrate  
Run #1 - May 23, 1950  
Mass of sample: 23.43 gm.

Temp. (°K)	K	$10^{13} \alpha$	$R_3$ (ohms)	Temp. (°K)	K	$10^{13} \alpha$	$R_3$ (ohms)
118.4	2.6811	10.051	2580	195.8	3.6458	13.115	2800
120.8	2.6911	10.086	2640	197.1	3.6471	13.118	2790
126.4	2.7082	10.154	2680	198.7	3.6418	13.104	2800
130.6	2.7295	10.234	2700	200.0	3.6381	13.095	2800
134.6	2.7516	10.316	2700	201.6	3.6337	13.083	2810
139.1	2.7658	10.369	2700	203.2	3.6261	13.063	2810
142.9	2.7772	10.411	2700	204.8	3.6193	13.045	2810
147.6	2.7910	10.462	2670	206.4	3.6156	13.035	2820
151.9	2.8142	10.546	2680	207.8	3.6085	13.016	2820
155.2	2.8324	10.612	2700	211.0	3.5980	12.988	2820
159.0	2.8563	10.698	2710	213.9	3.5851	12.954	2840
162.5	2.8804	10.783	2730	215.6	3.5807	12.942	2850
166.2	2.9231	10.932	2750	219.1	3.5717	12.922	2860
169.0	2.9650	11.076	2790	222.4	3.5656	12.896	2870
172.3	3.0243	11.276	2790	240.9	3.5468	12.850	3020
174.2	3.1111	11.559	2790	242.7	3.5490	12.856	3060
175.9	3.1700	11.747	2800	245.4	3.5579	12.880	3090
177.6	3.2410	11.966	2800	248.1	3.5656	12.901	3150
181.0	3.3003	12.146	2810	251.0	3.5794	12.938	3230
182.6	3.3704	12.352	2810	253.6	3.5910	13.019	3310
184.2	3.4399	12.552	2820	256.0	3.6042	13.028	3410
185.8	3.5104	12.750	2850	258.6	3.6177	13.041	3530
187.8	3.4826	12.572	2830	261.2	3.6337	13.083	3690
189.4	3.5172	12.769	2850	262.9	3.6651	13.166	3860
191.0	3.6230	13.055	2850	265.9	3.6758	13.194	4050
192.6	3.6381	13.095	2790	268.7	3.7023	13.263	4260
194.2	3.6418	13.115	2800				



Chromium Sulphate Hydrate  
Run #2(a) - June 24, 1950  
Mass of sample 25.110 gm.

Temp. (°K)	K	$10^{23}$ $10^6 \Omega$	$R_3$ (ohms)	Temp. (°K)	K	$10^{23}$ $10^6 \Omega$	$R_3$ (ohms)
289.7	4.9897	14.906	8870	226.0	3.9766	13.006	2993
288.2	4.8789	14.725	8230	224.3	3.9781	13.009	2985
285.7	4.7529	14.513	7610	223.0	3.9803	13.014	2930
282.7	4.5586	14.169	6810	221.4	3.9831	13.020	2968
280.2	4.4688	14.003	6290	221.0	3.9890	13.033	2960
278.2	4.3850	13.846	5820	219.5	3.9919	13.039	2960
275.2	4.3393	13.756	5540	218.3	3.9956	13.047	2960
273.0	4.2940	13.667	5240	216.8	4.0007	13.058	2957
270.0	4.2396	13.558	4920	215.2	4.0057	13.069	2955
268.2	4.2072	13.493	4690	213.9	4.0088	13.076	2953
265.9	4.1787	13.434	4450	212.3	4.0233	13.083	2951
263.2	4.1437	13.362	4173	210.5	4.0182	13.096	2940
260.2	4.1205	13.314	3992	209.0	4.0276	13.117	2960
259.0	4.0997	13.270	3800	207.8	4.0350	13.133	2980
255.1	4.0686	13.204	3585	206.1	4.0386	13.140	2967
253.3	4.0604	13.187	3535	204.8	4.0445	13.153	2965
251.0	4.0429	13.150	3420	203.2	4.0510	13.167	2935
248.1	4.0291	13.120	3336	201.3	4.0576	13.181	2930
245.4	4.0175	13.095	3268	200.0	4.0686	13.204	2940
242.4	4.0007	13.058	3197	198.4	4.0758	13.220	2926
239.9	3.9934	13.042	3148	196.8	4.0780	13.224	2907
237.4	3.9838	13.022	3104	195.8	4.0830	13.235	2900
234.5	3.9774	13.007	3068	193.9	4.0867	13.243	2900
232.5	3.9759	13.004	3040	192.3	4.0883	13.246	2900
229.6	3.9744	13.001	3006	190.7	4.0830	13.235	2905



Chromium Sulphate Hydrate  
Run #2(a) - continued.

Temp. (°K)	K	$\frac{10^3}{10^2} \alpha$	R <sub>2</sub> (ohms)
189.0	4.0576	13.181	2900
187.5	4.0219	13.104	2910
185.5	3.9378	12.920	2910
183.9	3.8528	12.728	2910
182.9	3.8188	12.650	2915
181.3	3.7483	12.485	2914
179.7	3.6727	12.303	2919
178.1	3.5993	12.122	2919
176.8	3.5619	12.028	2929
173.9	3.4521	11.745	2904
167.9	3.3363	11.433	2904
167.6	3.3183	11.383	2900
164.1	3.2679	11.242	2890
158.5	3.2265	11.124	2880
154.9	3.1928	11.027	2880
150.8	3.1656	10.948	2870
147.3	3.1426	10.880	2870
143.3	3.1222	10.819	2871
139.1	3.0999	10.752	2870
140.0	3.1084	10.778	2870
135.3	3.0898	10.722	2890
130.9	3.0734	10.672	2910
125.9	3.0432	10.580	2930
120.3	3.0123	10.484	2920



Chromium Sulphate Hydrate  
Run #2(b) - June 24, 1950.  
Mass of sample 25.110 gm.

Temp. (°K)	K	<sup>13</sup> 10 Ω	R <sub>3</sub> (ohms)	Temp. (°K)	K	<sup>13</sup> 10 Ω	R <sub>3</sub> (ohms)
129.1	3.0683	10.656	2900	195.5	4.0714	13.210	2910
131.5	3.0813	10.695	2887	196.8	4.0664	13.199	2905
135.3	3.0949	10.737	2907	198.1	4.0612	13.189	2705
139.5	3.1128	10.791	2894	199.7	4.0517	13.168	2905
143.4	3.1273	10.835	2867	201.3	4.0416	13.147	2905
147.0	3.1470	10.893	2870	201.9	4.0357	13.134	2905
151.1	3.1709	10.963	2870	204.5	4.0291	13.120	2905
154.9	3.1978	11.042	2865	205.9	2.0219	13.104	2905
158.1	3.2223	11.112	2870	207.4	4.0175	13.095	2905
162.2	3.2526	11.199	2874	208.7	4.0116	13.082	2905
165.4	3.3054	11.347	2910	210.5	4.0044	13.066	2900
170.7	3.3759	11.539	2905	213.6	3.9934	13.042	2920
172.8	3.4313	11.690	2915	216.8	3.9890	13.033	2925
174.2	3.4927	11.851	2915	219.8	3.9803	13.014	2935
175.5	3.5430	11.980	2915	222.7	3.9737	12.999	2950
177.6	3.6237	12.183	2905	225.7	3.9693	12.990	2970
179.7	3.6576	12.267	2901	229.4	3.9665	12.983	2995
180.7	3.7014	12.373	2901	230.8	3.9665	12.983	3015
182.0	3.7770	12.553	2895	233.2	3.9643	12.979	3015
185.2	3.9233	12.888	2895	236.0	3.9656	12.982	3050
187.1	4.0072	13.072	2900	238.7	3.9671	12.985	3065
188.4	4.0467	13.158	2895	241.1	3.9752	13.002	3130
190.4	4.0699	13.207	2885	244.4	3.9875	13.030	3210
191.6	4.0751	13.218	2915	247.4	4.0013	13.060	3290
193.6	4.0780	13.224	2915	249.6	4.0131	13.085	3340



Chromium Sulphate Hydrate  
Run #2(b) - June 24, 1950  
Mass of sample 25.110 gm.

Temp. (°K)	K	$10^{23} \alpha$	R <sub>3</sub> (ohms)
252.3	4.0298	13.121	3450
255.0	4.0583	13.182	3590
257.3	4.0758	13.220	3700
259.9	4.1005	13.272	3860
262.2	4.1330	13.340	4070
264.0	4.1555	13.387	4250
265.4	4.1779	13.433	4440
267.4	4.2186	13.518	4720
270.7	4.2620	13.603	5000
273.5	4.3174	13.712	5390
276.5	4.3654	13.806	5700
278.9	4.4311	13.932	6060
282.2	4.5437	14.142	6730



Chromium Sulphate Hydrate  
Run #3 - June 28, 1950.  
Mass of sample 25.110 gm.

Temp. (°K)	K	<sup>23</sup> 10 Ω	R <sub>3</sub> (ohms)	Temp. (°K)	K	<sup>23</sup> 10 Ω	R <sub>3</sub> (ohms)
113.7	2.9903	10.415	2950	190.4	4.0986	13.268	2980
118.0	3.0100	10.477	2990	192.3	4.1133	13.299	2980
123.1	3.0333	10.549	3010	193.9	4.1133	13.299	2980
126.8	3.0607	10.633	3000	195.2	4.1076	13.287	2980
131.5	3.0819	10.698	2870	196.8	4.1041	13.285	2990
135.8	3.1023	10.760	2960	198.4	4.0992	13.269	2990
140.3	3.1170	10.804	2950	200.0	4.0907	13.251	2990
144.1	3.1380	10.866	2960	201.3	4.0846	13.238	3000
148.9	3.1573	10.923	2960	203.2	4.0747	13.217	3000
152.7	3.1785	10.985	2960	204.5	4.0690	13.205	3000
155.5	3.2037	11.059	2970	205.8	4.0613	13.189	3000
158.5	3.2352	11.149	2980	207.4	4.0533	13.172	3000
162.5	3.2795	11.275	2980	212.3	4.0339	13.134	3000
165.7	3.3306	11.417	2990	217.1	2.0140	13.087	3040
169.0	3.3864	11.569	2990	219.5	4.0081	13.074	3050
173.3	3.5034	11.879	3000	221.2	4.0031	13.064	3060
174.5	3.5525	12.004	3000	225.4	3.9965	13.049	3100
177.1	3.6850	12.333	3000	228.3	3.9934	13.042	3140
179.4	3.7525	12.495	2990	231.2	3.9702	12.991	3300
180.7	3.8572	12.738	2990	233.5	3.9899	13.035	3280
183.6	3.9257	12.893	2990	236.0	3.9818	13.017	3240
184.6	3.9893	13.034	2990	240.7	3.9899	13.035	3120
185.8	4.0344	13.131	2980	241.9	3.9956	13.047	3110
187.5	4.0712	13.210	2980	244.4	4.0031	13.064	3170
189.0	4.0986	13.268	2980	249.3	4.0285	13.118	3320



Chromium Sulphate Hydrate  
Run #3 - June 28, 1950.  
Mass of sample 25.110 gm.

Temp. (°K)	K	$\frac{R_3}{10 \Omega}$	R <sub>3</sub> (ohms)
251.8	4.0460	13.156	3420
254.8	4.0655	13.198	3550
255.3	4.0735	13.213	3640
258.5	4.0964	13.263	3810
260.5	4.1238	13.321	4050
263.0	4.1461	13.367	4190
2654	4.1636	13.403	4370
268.2	4.2028	13.484	4700
270.7	4.2416	13.562	5010
272.2	4.2931	13.665	5340
276.2	4.3200	13.718	5550
279.5	4.4134	13.898	5920
280.9	4.5005	14.062	6920
283.7	4.5812	14.210	6880
285.5	4.6813	14.388	7400
287.9	4.7901	14.576	7980
289.9	4.9165	14.787	8630
291.9	5.0769	15.044	9330



Anhydrous Chromium Sulphate  
Run #1 - May 29, 1950.  
Mass of sample 31.56 gm.

Temp. (°K)	K	$\frac{10}{10^\circ \text{C}}$	R <sub>2</sub> (ohms)	Temp. (°K)	K	$\frac{10}{10^\circ \text{C}}$	R <sub>2</sub> (ohms)
118.1	2.3860	3.5283	2653	205.1	2.5161	3.7482	2963
123.1	2.3869	3.5298	2659	207.8	2.5358	3.7805	3015
127.8	2.3893	3.5339	2668	211.0	2.5586	3.8173	3070
131.8	2.3904	3.5358	2673	214.6	2.5886	3.8654	3168
136.2	2.3936	3.5414	2680	218.3	2.6396	3.9457	3348
140.0	2.3956	3.5449	2687	220.1	2.6852	4.0159	3400
144.3	2.3993	3.5513	2693	222.7	2.6938	4.0290	2540
147.6	2.4009	3.5540	2699	226.0	2.7516	4.1158	3740
151.4	2.4046	3.5504	2704	228.6	2.8149	4.2084	3955
155.7	2.4079	3.5661	2709	231.5	2.8701	4.2874	4110
159.0	2.4101	3.5699	2716	234.2	2.9704	4.4261	4390
162.5	2.4145	3.5775	2723	237.1	3.0519	4.5348	4710
166.6	2.4169	3.5816	2732	239.9	3.1700	4.6863	5040
170.1	2.4228	3.5918	2744				
173.3	2.4261	3.5988	2754				
176.5	2.4313	3.6063	2760				
180.0	2.4357	3.6141	2770				
183.2	2.4438	3.6275	2784				
186.8	2.4497	3.6376	2800				
189.7	2.4570	3.6498	2812				
192.9	2.4657	3.6645	2829				
195.8	2.4756	3.6811	2856				
198.7	2.4878	3.7014	2880				
201.9	2.5019	3.7248	2920				



Anhydrous Chromium Sulphate  
Run #2(a) - July 24, 1950.  
Mass of sample 24.761 gm.

Temp. (°K)	K	$\frac{23}{10^\circ \text{C}}$	$R_2$ (ohms)	Temp. (°K)	K	$\frac{23}{10^\circ \text{C}}$	$R_2$ (ohms)
296.9	2.7816	5.589	6740	234.0	2.0804	3.972	3780
296.9	2.7665	5.559	6690	230.2	2.0760	3.960	3770
292.9	2.6911	5.407	6380	227.6	2.0692	3.941	3740
290.2	2.6486	5.320	6210	225.7	2.0602	3.917	3710
286.19	2.6068	5.230	6060	222.4	2.0526	3.896	3690
285.7	2.5652	5.143	5940	219.5	2.0480	3.884	3670
281.0	2.4856	4.968	5630	216.5	2.0366	3.852	3640
277.0	2.4427	4.871	5450	214.2	2.0335	3.843	3640
273.2	2.3939	4.759	5220	210.5	2.0308	3.808	3580
270.9	2.3689	4.700	5110	207.8	2.0230	3.814	3580
267.9	2.3338	4.617	4990	204.5	2.0171	3.798	3580
265.7	2.3019	4.539	4860	201.3	2.0156	3.794	3580
263.5	2.2806	4.487	4760	198.1	2.0094	3.776	3550
260.5	2.2515	4.416	4630	195.8	2.0011	3.753	3550
258.3	2.2304	4.363	4530	192.3	1.9989	3.747	3550
256.3	2.2120	4.316	4420	190.0	1.9982	3.745	3530
255.0	2.1912	4.263	4330	185.8	1.9899	3.722	3520
251.9	2.1746	4.221	4230	183.2	1.9893	3.720	3520
249.8	2.1617	4.187	4160	180.3	1.9893	3.720	3500
247.1	2.1441	4.141	4070	176.9	1.9783	3.692	3480
245.1	2.1343	4.115	4010	173.9	1.9768	3.684	3470
242.4	2.1170	4.070	3980	171.1	1.9768	3.684	3470
239.4	2.1034	4.034	3910	167.6	1.9768	3.684	3470
236.5	2.0911	4.000	3830	162.2	1.9761	3.682	3500



Anhydrous Chromium Sulphate  
Run #2(a) - July 24, 1950  
Mass of sample 24.761 gm.

Temp. (°K)	K	$10 \alpha$	$R_3$ (ohms)
161.9	1.9761	3.682	3500
156.5	1.9755	3.681	3500
150.5	1.9702	3.666	3490
147.5	1.9717	3.670	3480
147.3	1.9663	3.654	3480
143.4	1.9663	3.654	3480
135.3	1.9625	3.644	3480
131.8	1.9604	3.638	3470
127.3	1.9579	3.630	3470
123.1	1.9579	3.630	3460
117.5	1.9551	3.622	3470
112.4	1.9551	3.622	3470



Anhydrous Chromium Sulphate  
Run #2(b) - July 24, 1950.  
Mass of sample 24.761 gm.

Temp. (°K)	K	$\frac{10^{23}}{10^6 \Omega}$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$\frac{10^{23}}{10^6 \Omega}$	R <sub>3</sub> (ohms)
110.9	1.9527	3.615	3470	202.2	2.0125	3.785	3550
115.6	1.9551	3.622	3470	205.6	2.0162	3.795	3570
119.3	1.9551	3.622	3470	208.1	2.0199	3.806	3610
127.8	1.9537	3.629	3470	211.7	2.0283	3.834	3620
131.5	1.9610	3.639	3470	214.6	2.0344	3.846	3600
135.8	1.9604	3.638	3480	216.8	2.0381	3.856	3610
140.0	1.9610	3.639	3470	219.5	2.0629	3.924	3600
143.8	1.9650	3.651	3480	222.5	2.0510	3.899	3620
148.1	1.9650	3.651	3480	225.4	2.0602	3.917	3640
151.4	1.9617	3.641	3470	228.6	2.0653	3.931	3650
154.9	1.9656	3.652	3470	231.5	2.0721	3.949	3660
158.5	1.9739	3.676	3490	235.2	2.0867	3.989	3760
162.5	1.9739	3.676	3480	236.8	2.0929	4.005	3780
166.6	1.9739	3.676	3490	238.7	2.1027	4.032	3830
169.5	1.9763	3.683	3490	241.7	2.1154	4.065	3890
172.8	1.9792	3.691	3490	244.1	2.1284	4.100	3960
176.2	1.9798	3.693	3480	246.9	2.1426	4.137	4030
179.7	1.9838	3.704	3490	249.3	2.1562	4.137	4090
182.6	1.9860	3.711	3490	251.6	2.1724	4.215	4170
185.5	1.9897	3.721	3500	252.6	2.1888	4.257	4230
189.0	1.9919	3.727	3500	255.3	2.2116	4.315	4350
192.9	1.9996	3.749	3520	258.3	2.2405	4.388	4490
196.0	2.0002	3.750	3520	259.9	2.2600	4.452	4590
198.7	2.0066	3.786	3540	262.7	2.2878	4.505	4730



Anhydrous Chromium Sulphate  
Run #2(b) - July 24, 1950  
Mass of sample - 24.761 gm.

Temp. (°K)	K	$10^{23} \alpha$	R <sub>3</sub> (ohms)
265.5	2.3157	4.573	4880
267.9	2.3514	4.651	5030
271.2	2.3952	4.762	5210
273.5	2.4357	4.855	5400
2757	2.4778	4.950	5600
278.9	2.5382	5.084	5880
283.5	2.6460	5.314	6030
283.5	2.6396	5.300	6300
284.7	2.6821	5.389	6580
283.7	2.6883	5.402	6530
283.5	2.7073	5.440	6600
283.7	2.7809	5.588	6900
286.9	2.8541	5.730	7190
288.7	2.9450	5.900	7570



Anhydrous Chromium Sulphate  
Run #3 July 26, 1950.  
Mass of sample 24.761 gm.

Temp. (°K)	K	$10 \frac{23}{\alpha}$	$R_3$ (ohms)	Temp. (°K)	K	$10 \frac{23}{\alpha}$	$R_3$ (ohms)
262.9	3.5748	6.928	10330	196.8	2.0193	3.804	3510
260.5	3.4204	6.698	9780	191.6	2.0039	3.761	3480
257.0	3.2867	6.488	9160	189.7	2.0116	3.783	3440
254.0	3.1428	6.250	8570	186.8	2.0055	3.765	3430
251.0	3.0094	6.017	8000	182.9	1.9996	3.749	3420
247.9	2.8878	5.793	7520	180.3	1.9963	3.740	3410
245.1	2.8004	5.626	7100	176.8	1.9912	3.725	3370
241.9	2.6815	5.388	6600	174.2	1.9866	3.712	3360
239.4	2.5952	5.207	6200	171.7	1.9860	3.710	3360
238.8	2.5229	5.051	5940				
232.8	2.4353	4.854	5510				
231.8	2.3974	4.767	5310				
228.3	2.3148	4.571	4950				
224.7	2.2662	4.452	4670				
222.4	2.2226	4.343	4500				
220.1	2.1860	4.250	4320				
216.8	2.1540	4.167	4140				
214.2	2.1246	4.090	4000				
211.7	2.1027	4.032	3900				
208.7	2.0852	3.985	3800				
206.1	2.0642	3.928	3670				
202.2	2.0381	3.856	3600				
198.7	2.0285	3.830	3550				



Anhydrous Chromium Sulphate  
Run #4 - August 1, 1950.  
Mass of sample 29,598 gm.

Temp. (°K)	K	$10 \frac{13}{\alpha}$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$10 \frac{13}{\alpha}$	R <sub>3</sub> (ohms)
101.7	2.0745	3.309	3000	207.1	2.1770	3.536	3350
101.2	2.0778	3.317	3020	210.0	2.1930	3.570	3420
109.6	2.0799	3.322	3030	213.4	2.2072	3.601	3500
114.7	2.0806	3.323	3040	215.9	2.2276	3.644	3610
119.0	2.0806	3.325	3040	218.8	2.2499	3.691	3730
124.0	2.0852	3.334	3060	221.4	2.2719	3.736	3860
132.0	2.0874	3.339	3070	224.7	2.2997	3.793	4010
136.2	2.0889	3.342	3080	227.3	2.3200	3.835	4110
140.3	2.0913	3.347	3090	320.2	2.3463	3.887	4290
154.3	2.1003	3.368	3090	232.8	2.3739	3.942	4450
156.5	2.1043	3.376	3100	235.8	2.4177	4.027	4700
160.9	2.1065	3.381	3100	238.7	2.4584	4.105	4970
164.7	2.1065	3.381	3080	241.1	2.5012	4.185	5220
166.6	2.1095	3.388	3090	243.7	2.5772	4.324	5700
170.1	2.1133	3.397	3100	246.7	2.6344	4.426	6000
173.9	2.1141	3.398	3090	249.3	2.7179	4.569	6490
177.6	2.1225	3.417	3110	252.0	2.7761	4.667	6820
181.0	2.1240	3.420	3100	255.3	2.8806	4.835	7400
188.1	2.1330	3.440	3140	257.3	2.9967	5.015	8020
190.7	2.1376	3.450	3150	260.2	3.1216	5.198	8720
193.9	2.1428	3.462	3170	262.9	3.2340	5.354	9320
196.8	2.1481	3.473	3190	265.7	3.3886	5.563	9750
200.6	2.1555	3.489	3240	267.2	3.4609	5.655	10700
203.9	2.1656	3.511	3290				



Nickel Nitrate  
Run #1(a) - August 3, 1950  
Mass of sample 30.403 gm.

Temp. (°K)	K	<sup>23</sup> 10 <sup>3</sup> $\alpha$	R <sub>3</sub> (ohms)	Temp. (°K)	K	<sup>23</sup> 10 <sup>3</sup> $\alpha$	R <sub>3</sub> (ohms)
102.6	2.4114	2.898	3260	194.8	2.5465	3.081	3360
106.3	2.4114	2.898	3270	197.7	2.5667	3.108	3400
110.0	2.4162	2.905	3270	201.0	2.5798	3.125	3440
115.2	2.4212	2.912	3270	204.2	2.5812	3.126	3450
119.8	2.4256	2.918	3280	207.1	2.5923	3.141	3480
124.0	2.4333	2.928	3290	210.3	2.6068	3.159	3560
128.3	2.4458	2.946	3290	213.1	2.6280	3.185	3680
133.4	2.4375	2.934	3280	215.9	2.6609	3.228	3850
137.2	2.4563	2.960	3300	218.1	2.6995	3.276	4040
143.8	2.4515	2.952	3290	221.3	2.7698	3.361	4360
145.7	2.4528	2.955	3290	225.0	2.8675	2.475	4760
148.9	2.4550	2.958	3280	227.6	3.0094	3.633	5170
152.7	2.4611	2.967	3290	229.1	3.1853	3.817	5900
155.5	2.4668	2.974	3290	229.9	3.3091	3.940	6640
161.6	2.4751	2.986	3300	231.8	3.5527	4.164	8100
163.8	2.4793	2.991	3300				
168.2	2.4870	3.022	3300				
170.7	2.4935	3.011	3310				
174.2	2.4955	3.013	3310				
178.1	2.5019	3.022	3300				
181.0	2.5102	3.033	3310				
184.9	2.5207	3.047	3320				
188.1	2.5312	3.061	3340				
191.6	2.5395	3.072	3340				



Nickel Nitrate  
Run #1(b) - August 3, 1950.  
Mass of sample 30.403 gm.

Temp. (°K)	K	$10 \alpha^{23}$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$10 \alpha^{23}$	R <sub>3</sub> (ohms)
110.9	2.4085	2.894	3320	191.3	2.5277	3.056	3350
115.0	2.4136	2.901	3320	194.5	2.5389	3.071	3370
119.8	2.4199	2.910	3320	197.4	2.5461	3.081	3400
124.0	2.4232	2.915	3320	200.6	2.5562	3.094	3410
129.6	2.4283	2.922	3320	206.8	2.5785	3.123	3490
134.3	2.4324	2.927	3320	209.0	2.5965	3.146	3550
138.1	2.4386	2.936	3320	212.3	2.6217	3.178	3560
141.0	2.4435	2.943	3320	215.6	2.6581	3.224	3830
145.1	2.4493	2.951	3320	218.5	2.7034	3.2804	4000
148.3	2.4510	2.953	3320	221.7	2.7685	3.359	4290
151.7	2.4585	2.963	3320	223.9	2.8714	3.480	4750
155.5	2.4605	2.966	3320	227.9	3.1518	3.783	5770
160.5	2.4620	2.968	3310	230.8	3.4248	4.067	7520
163.8	2.4703	2.979	3320	231.5	3.5884	4.195	8480
168.5	2.4773	2.989	3320				
171.1	2.4843	2.989	3320				
174.5	2.4885	3.004	3320				
178.8	2.4933	3.010	3330				
181.3	2.5016	3.021	3330				
184.2	2.5124	3.036	3340				
187.5	2.5192	3.045	3350				



Nickel Nitrate  
Run #2(a) - August 9, 1950.  
Mass of sample 28.528 gm.

Temp. (°K)	K	<sup>23</sup> 10 $\alpha$	R <sub>3</sub> (ohms)	Temp. (°K)	K	<sup>23</sup> 10 $\alpha$	R <sub>3</sub> (ohms)
280.7	3.7349	4.603	7500	221.4	2.3871	3.052	3210
278.7	3.2304	4.116	5660	218.5	2.3827	3.045	3220
275.7	2.8386	3.668	4330	215.2	2.3728	3.030	3240
273.2	2.6968	3.487	3900	213.1	2.3693	3.025	3250
270.7	2.6252	3.392	3680	209.7	2.3595	3.010	3270
267.7	2.5650	3.428	3490	205.6	2.3367	2.975	3270
264.5	2.5220	3.249	2270	203.5	2.3054	2.927	3240
262.2	2.4964	3.213	3300	199.7	2.2651	2.863	3160
259.7	2.4729	3.179	3260	195.2	2.2386	2.821	3110
257.0	2.4528	3.149	3220	191.9	2.2300	2.807	3110
254.3	2.4329	3.120	3190	190.4	2.2138	2.781	3110
251.8	2.4245	3.108	3180	186.3	2.2094	2.773	3100
249.3	2.4162	2.095	3180	185.2	2.2059	2.768	3090
246.7	2.4061	3.081	3170	180.7	2.2011	2.760	3090
246.4	2.4118	3.089	3170	178.4	2.1993	2.757	3090
245.4	2.4079	3.083	3170	174.9	2.1917	2.744	3090
243.1	2.4044	3.078	3170	171.4	2.1840	2.732	3090
239.7	2.4020	3.074	3160	169.0	2.1840	2.732	3090
237.4	2.3978	3.068	3160	164.1	2.1709	2.710	3080
234.2	2.4061	3.081	3170	161.9	2.1685	2.706	3080
231.5	2.4020	2.074	3180	156.9	2.1610	2.693	3080
227.2	2.3978	3.068	3180	154.3	2.1582	2.689	3080
224.3	2.3945	3.063	3190	149.2	2.1533	2.680	3070



Nickel Nitrate  
Run #2(a) - August 9, 1950  
Mass of sample 28.528 gm.

Temp. (°K)	K	<sup>23</sup> 10 Ω	R <sub>3</sub> (ohms)
143.8	2.1465	2.669	3070
141.5	2.1457	2.668	3070
137.2	2.1409	2.660	3070
133.0	2.1382	2.655	3070
129.6	2.1338	2.648	3070
124.5	2.1297	2.641	3070
119.3	2.1240	2.631	3070
113.7	2.1181	2.621	3070
107.2	2.1104	2.608	3070



Nickel Nitrate  
Run #2(b) - August 9, 1950.  
Mass of sample 28.528 gm.

Temp. (°K)	K	$\frac{23}{10^\circ \text{C}}$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$\frac{23}{10^\circ \text{C}}$	R <sub>3</sub> (ohms)
104.9	2.1104	2.608	3070	184.9	2.2009	2.759	3050
109.5	2.1154	2.616	3070	188.3	2.2068	2.769	3050
113.3	2.1181	2.621	3070	190.7	2.2099	2.773	3050
118.4	2.1255	2.633	3070	194.5	2.2156	2.784	3050
123.1	2.1255	2.633	3070	197.4	2.2223	2.794	3060
127.8	2.1332	2.647	3070	200.6	2.2291	2.805	3070
132.5	2.1373	2.654	3070	203.9	2.2350	2.815	3090
136.2	2.1398	2.658	3070	215.2	2.2887	2.901	3240
140.3	2.1433	2.664	3060	221.3	2.3205	2.950	3300
143.8	2.1448	2.666	3060	225.0	2.3610	3.011	3400
147.3	2.1490	2.673	3040	227.3	2.4379	3.128	3400
152.4	2.1549	2.683	3040	230.2	2.4940	3.209	3400
155.7	2.1575	2.687	3050	233.2	2.5065	3.226	3420
159.0	2.1667	2.703	3050	236.2	2.5072	3.228	3470
162.2	2.1667	2.703	3050	238.4	2.5163	3.241	3500
165.7	2.1742	2.715	3050	242.7	2.5268	3.256	3540
169.8	2.1790	2.723	3050	243.7	2.5430	3.279	3560
172.8	2.1831	2.730	3050				
176.5	2.1881	2.738	3050				
181.0	2.1932	2.747	3050				



Chromium Nitrate  
Run #1(a) - August 28, 1950  
Mass of sample 25.466 gm.

Temp. (°K)	K	$\frac{23}{10} \alpha$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$\frac{23}{10} \alpha$	R <sub>3</sub> (ohms)
296.9	2.8388	5.6551	4480	235.2	2.4738	4.9024	3700
295.2	2.8055	5.5914	4360	232.2	2.4633	4.8789	3700
292.5	2.7514	5.4854	4180	229.3	2.4515	4.8524	3700
289.9	2.7137	5.4103	4030	226.6	2.4394	4.8250	3700
287.2	2.6725	5.3268	3940	223.7	2.4234	4.7889	3670
284.7	2.6425	5.2650	3850	220.5	2.4129	4.7696	3650
282.2	2.6204	5.2191	3780	216.2	2.3987	4.7320	3630
279.7	2.6004	5.1769	3740	214.6	2.3897	4.7112	3600
276.9	2.5843	5.1929	3700	211.7	2.3798	4.6882	3570
274.5	2.5737	5.1204	3680	208.7	2.3711	4.6678	3560
271.9	2.5647	5.1010	3670	204.8	2.3617	4.6458	3570
269.2	2.5542	5.0786	3660	202.2	2.3536	4.6269	3550
266.7	2.5501	5.0696	3650	199.7	2.349	4.6161	3550
263.9	2.5452	5.0591	3660	196.5	2.3389	4.5921	3550
261.7	2.5382	5.0441	3650	193.6	2.3338	4.5800	3550
259.2	2.5376	5.0427	3660	189.7	2.3279	4.5659	3530
256.6	2.5319	5.0304	3670	187.1	2.3257	4.5607	3520
253.7	2.5257	5.0168	3680	183.6	2.3207	4.5488	3510
251.7	2.5229	5.1017	3680	180.0	2.3192	4.5452	3510
248.4	2.5146	4.9926	3680	176.5	2.3148	4.5347	3510
246.7	2.5076	4.9772	3700	173.3	2.3113	4.5262	3500
240.9	2.4955	4.9506	3700	170.1	2.3076	4.5174	3500
238.1	2.4843	4.9257	3700	166.1	2.3076	4.5174	3490



Chromium Nitrate  
Run #1(a) - August 28, 1950  
Mass of sample 25.466 gm.

Temp. (°K)	K	$10^3 \alpha$	R <sub>2</sub> (ohms)
162.8	2.3010	4.5015	3490
159.0	2.3003	4.4997	3490
154.9	2.2968	4.4914	3490
152.9	2.2968	4.4914	3490
147.3	2.2924	4.4806	3490
143.3	2.2900	4.4748	3460
140.3	2.2872	4.4680	3460
136.7	2.2872	4.4680	3450
132.0	2.2843	4.4610	3450
129.6	2.2813	4.4537	3450
124.5	2.2778	4.4451	3450
119.3	2.2749	4.4381	3450
114.7	2.2712	4.4290	3450
108.6	2.2679	4.4253	3440
104.0	2.2646	4.4128	3440



Chromium Nitrate  
Run #1(b) - August 28, 1950  
Mass of sample 25.466 gm.

Temp. (°K)	K	$\frac{23}{10} \alpha$	R <sub>3</sub> (ohms)	Temp. (°K)	K	$\frac{23}{10} \alpha$	R <sub>3</sub> (ohms)
107.2	2.2644	4.4123	3450	203.5	2.3485	4.6149	3460
111.9	2.2675	4.4199	3450	206.1	2.3573	4.6556	3480
116.5	2.2681	4.4214	3450	209.7	2.3614	4.6452	3500
120.3	2.2719	4.4308	3460	212.7	2.3739	4.6744	3510
124.9	2.2740	4.4358	3440	215.6	2.3812	4.6948	3550
129.2	2.2762	4.4412	3440	219.1	2.3919	4.7129	3570
133.4	2.2806	4.4519	3440	221.4	2.4072	4.7516	3600
137.5	2.2821	4.4556	3440	230.5	2.9528	4.8554	3680
141.5	2.2857	4.4644	3440	230.5	2.4541	4.8582	3680
145.1	2.2850	4.4626	3430	233.8	2.4725	4.8994	3700
148.6	2.2906	4.4763	3440	236.2	2.4857	4.9289	3710
153.0	2.2938	4.4841	3440	239.4	2.4984	4.9570	3710
156.2	2.2938	4.4841	3440	241.7	2.5108	4.9842	3730
159.1	2.2981	4.4945	3460	244.4	2.5214	5.0074	3730
163.3	2.3025	4.5050	3450	246.7	2.5354	5.0379	3730
166.6	2.3069	4.5156	3450	249.3	2.5485	5.0662	3750
171.1	2.3089	4.5205	3450	251.8	2.5597	5.0903	3770
178.4	2.3148	4.5347	3450	255.3	2.5755	5.1567	3770
181.3	2.3185	4.5434	3450	257.3	2.5886	5.1196	3790
183.6	2.3200	4.5471	3450	260.5	2.5952	5.1659	3820
187.1	2.3214	4.5504	3450	262.7	2.6129	5.2033	3870
191.0	2.3273	4.5646	3450	265.7	2.6315	5.2421	3900
194.2	2.3317	4.5750	3460	268.5	2.6526	5.2859	3970
197.7	2.3382	4.5905	3460	271.2	2.6815	5.3451	4050
200.3	2.3439	4.6040	3460	273.2	2.7027	5.3881	4090



Ice

Data obtained from measurements of Dewar and Fleming

Temp. (°K)	K	$\frac{13}{10} \alpha$	Temp. (°K)	K	$\frac{13}{10} \alpha$
81.7	2.43	.231	212.3	46.8	.670
87.9	2.42	.229	220.8	55.8	.677
90.5	2.42	.229	226.2	57.2	.677
101.8	2.42	.229	235.5	58.9	.679
109.9	2.43	.231	239.5	58.5	.678
119.4	2.59	.247	247.2	59.2	.679
126.9	2.96	.282	249.8	59.1	.679
133.3	3.43	.320	251.7	59.1	.679
137.2	3.94	.353	253.1	61.3	.680
145.1	5.02	.409	256.4	61.3	.680
152.5	5.95	.445	259.0	65.4	.682
159.8	7.38	.485	263.5	67.8	.683
165.3	9.60	.529	266.4	70.8	.685
168.1	10.8	.547			
172.6	13.9	.579			
180.3	19.8	.615			
184.2	23.4	.630			
188.2	27.6	.642			
190.2	29.0	.645			
194.8	33.5	.653			
199.2	37.3	.660			
204.2	41.8	.665			



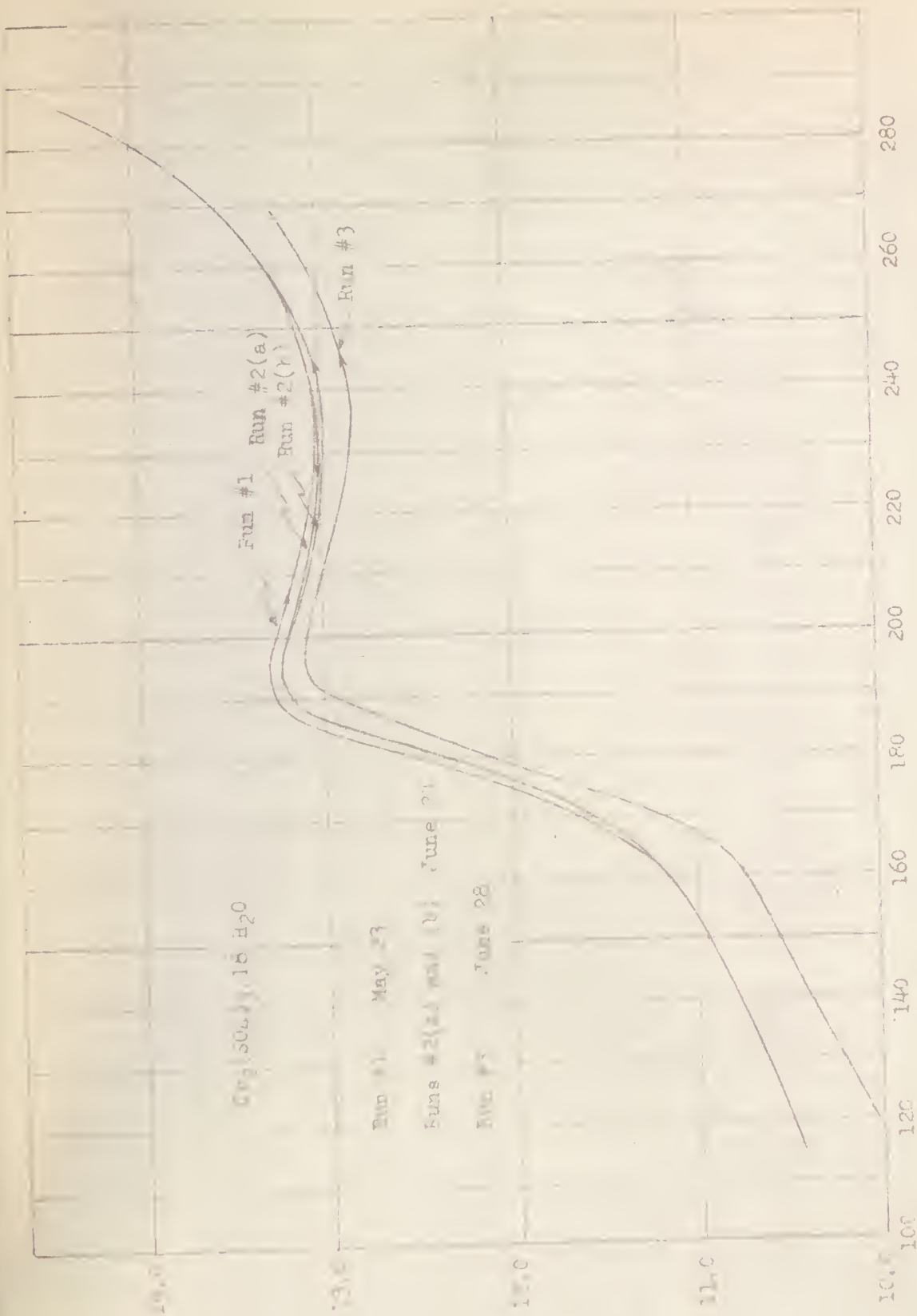


Figure 6 Polarizability,  $\alpha$ , against temperature for chromium sulphate hydrate



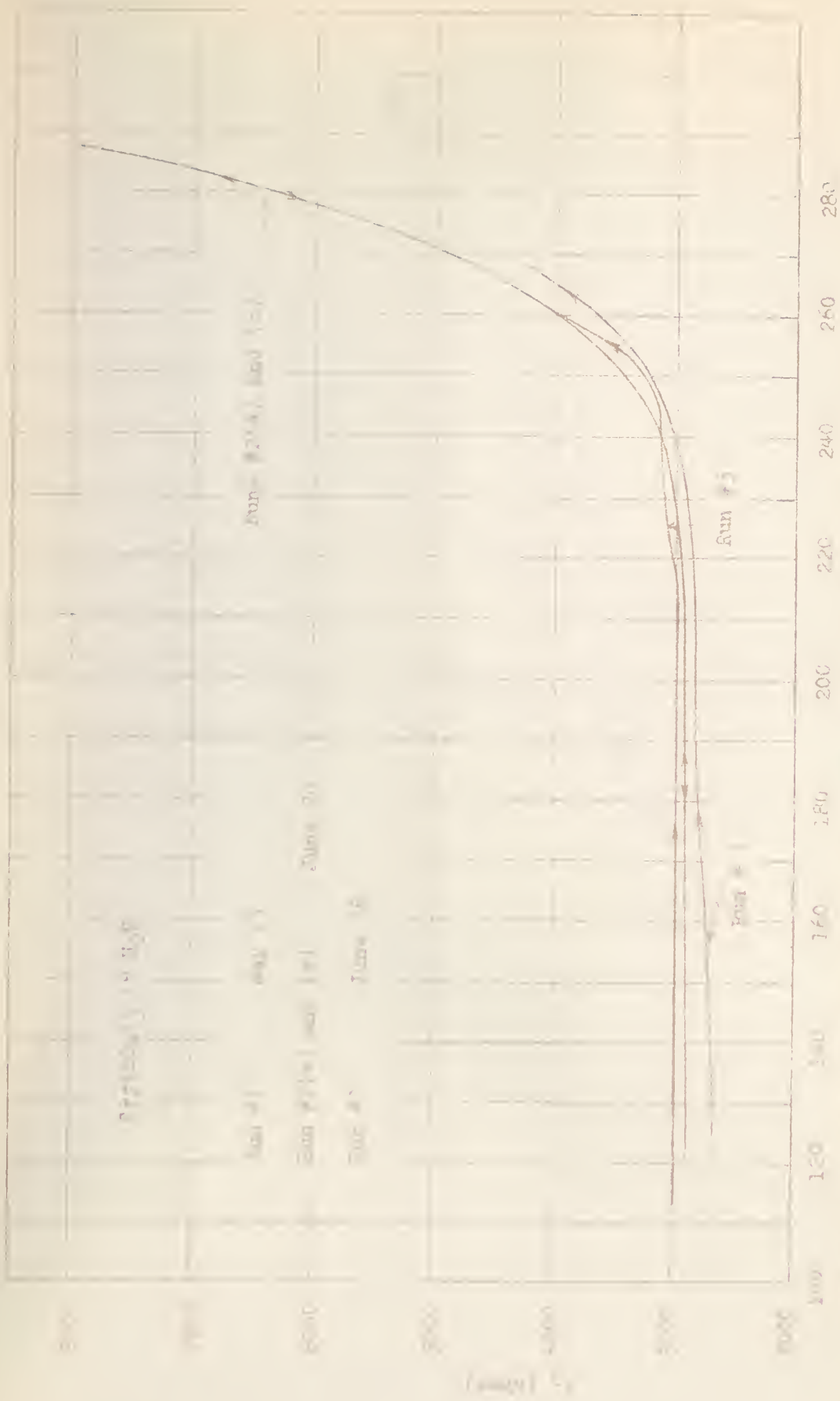


Figure 7 Variation of conductance with temperature for chromium sulphate hydrate



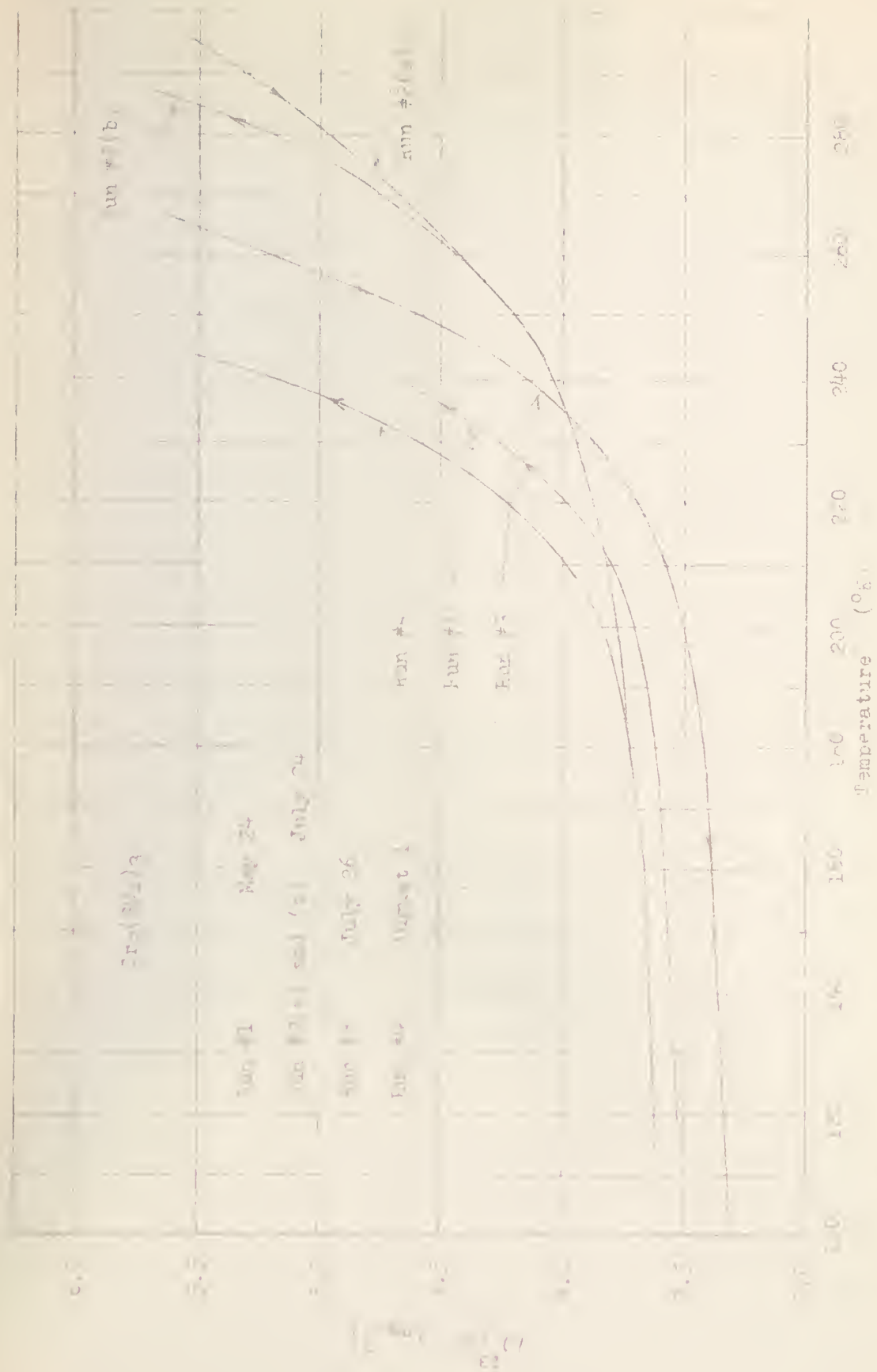


Figure 1 Polarizability,  $\alpha$ , against temperature for anhydrous chromium sulphate



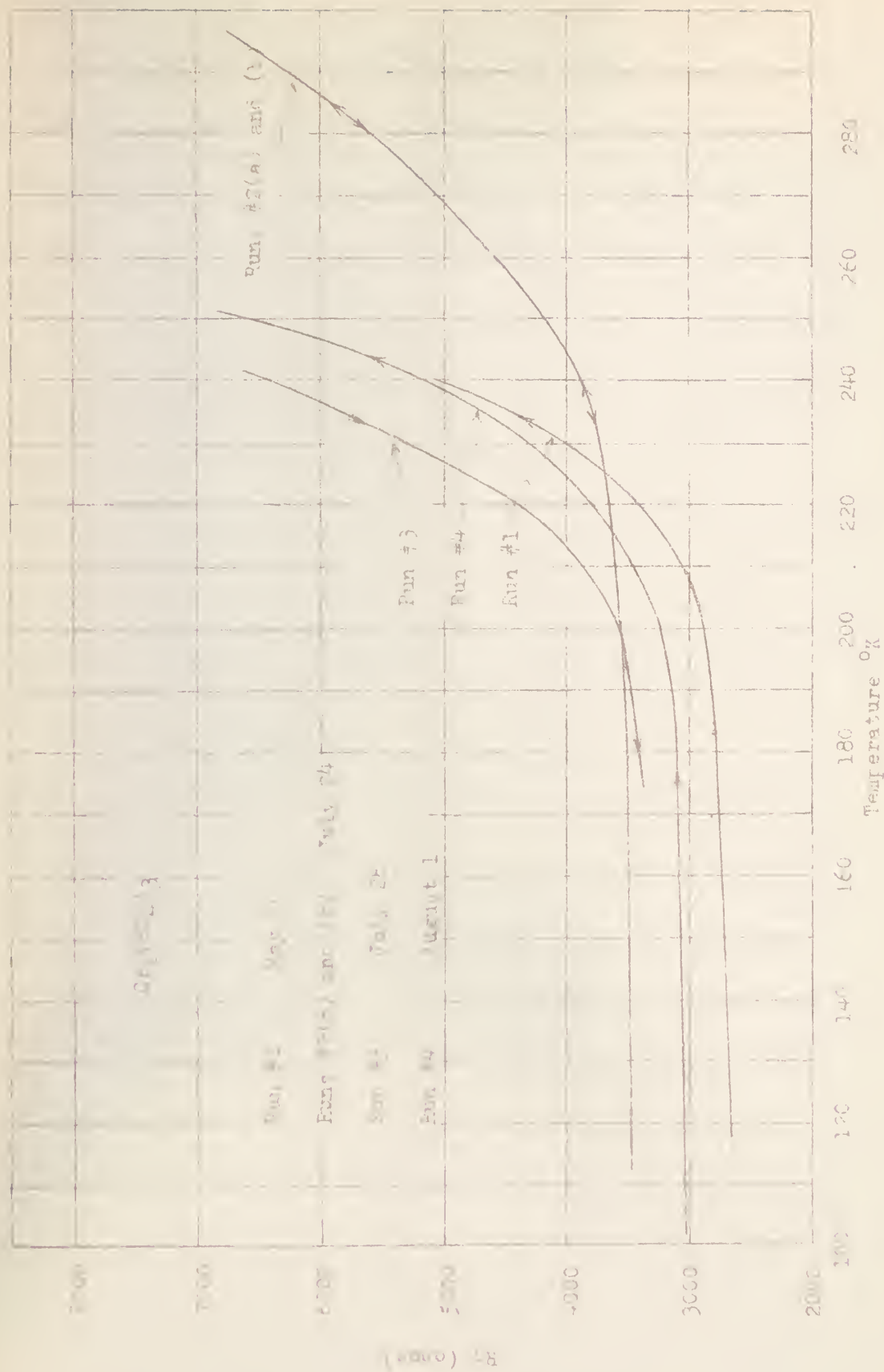


Figure 6 Variation of conductance with temperature for anhydrous chromium sulphate



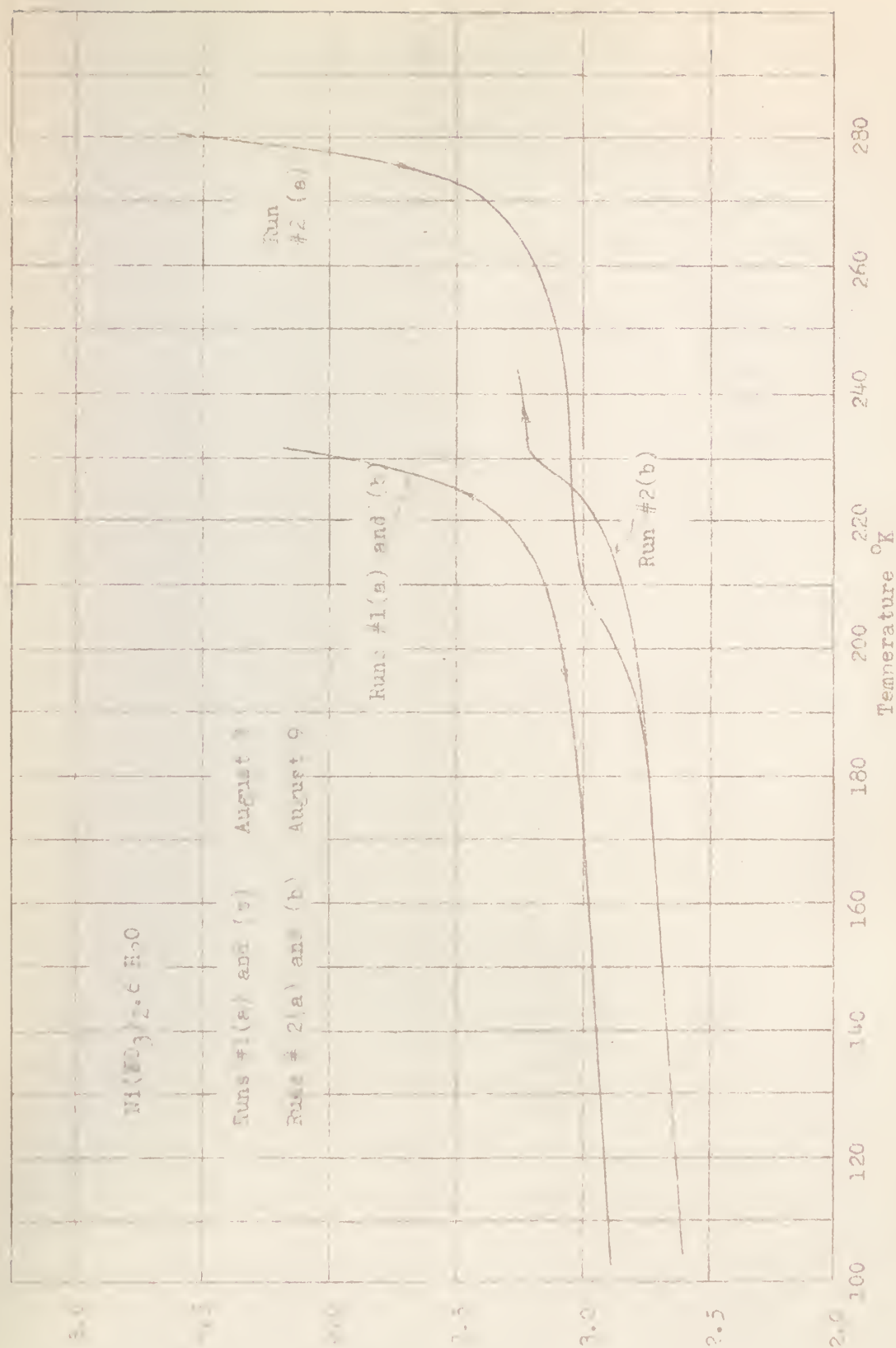


Figure 10 Polarizability,  $\alpha$ , against temperature for nickel nitrate



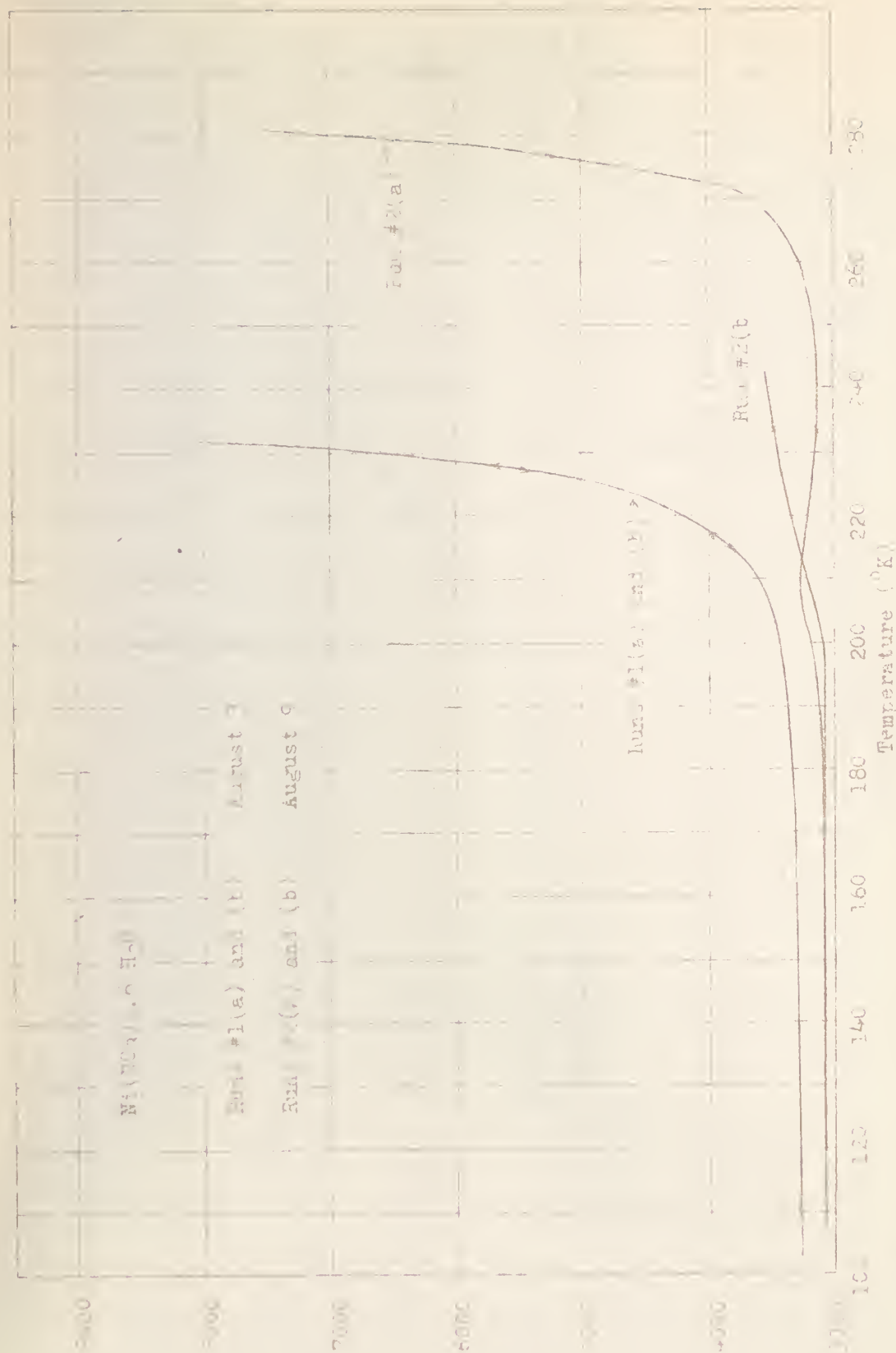


Figure 12 Variation of conductance with temperature for nickel nitrate



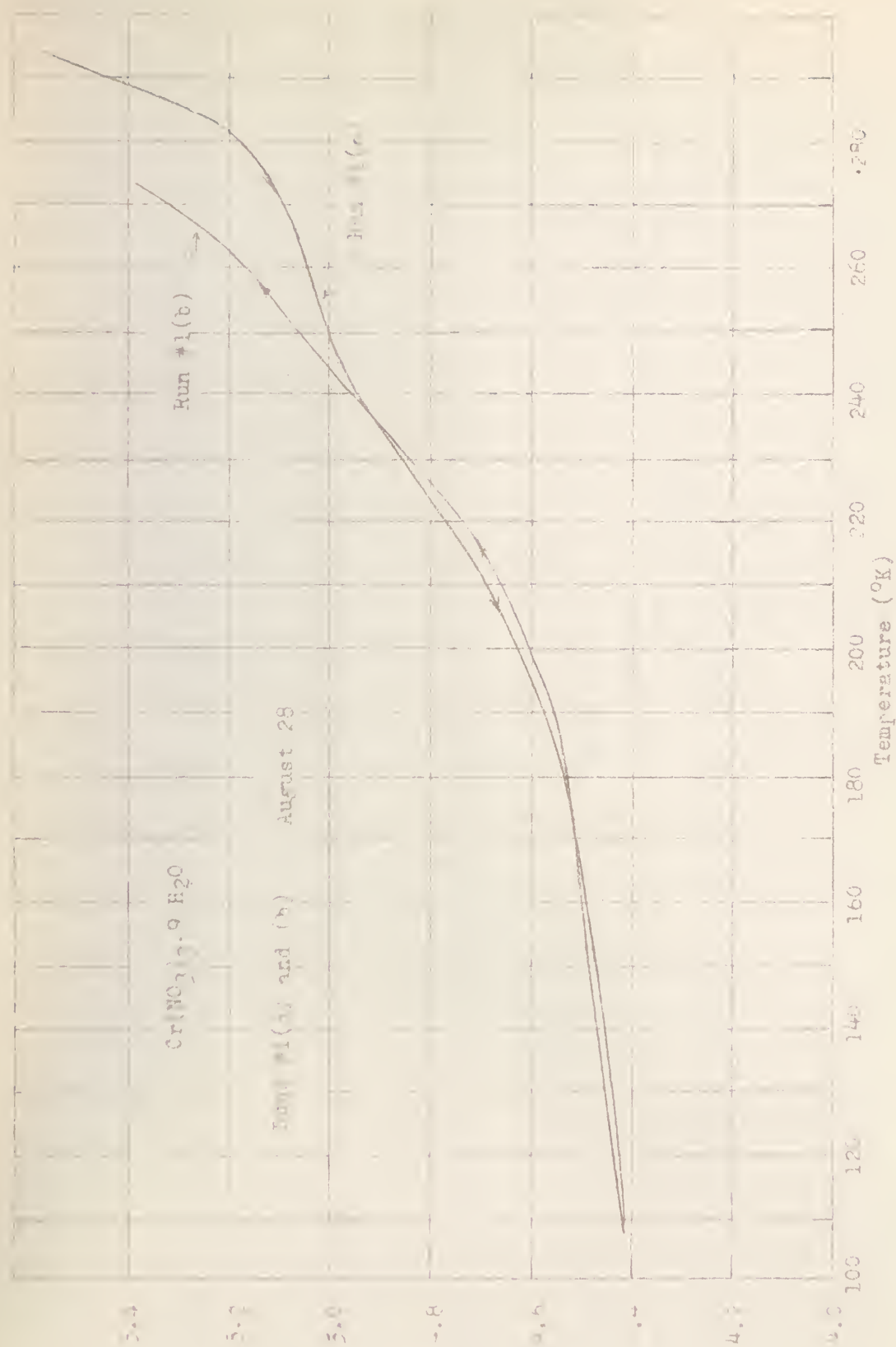


Figure 10 Polarizability,  $\alpha$ , against temperature for chromium nitrate



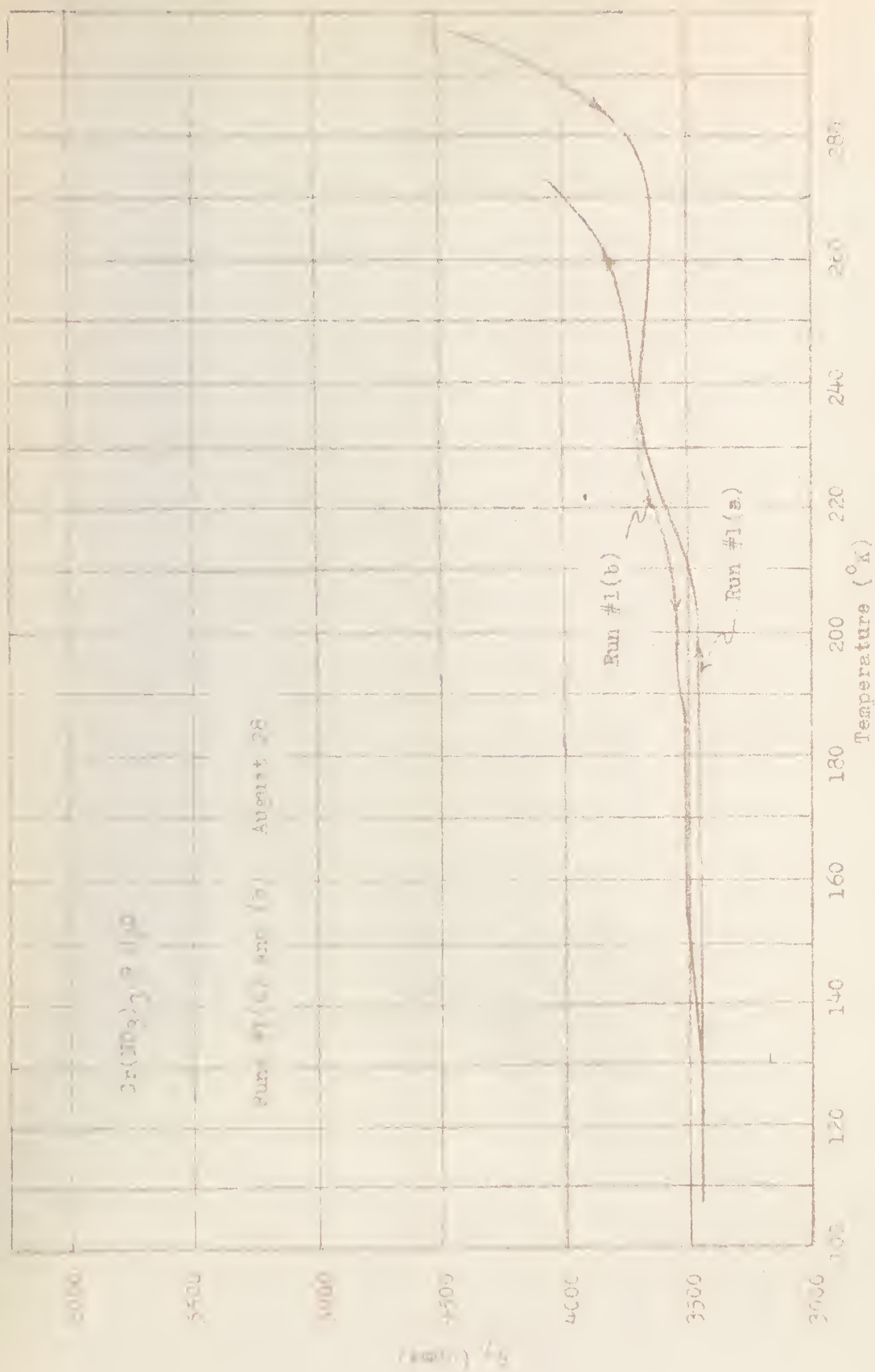
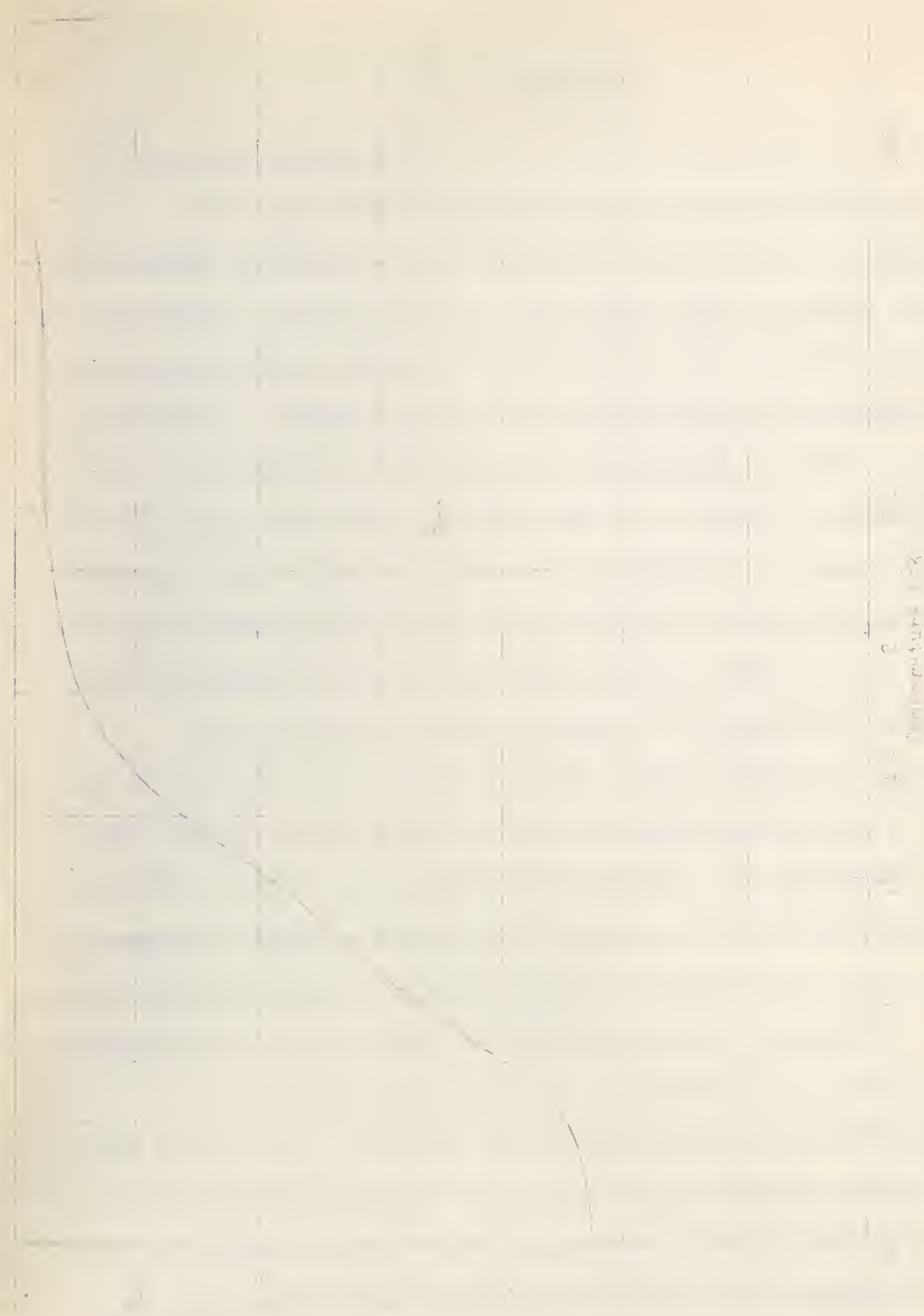


Figure 12 Variation of conductance with temperature for chromium nitrate





Graph of  $y = \log x$  for  $x > 0$   
The curve is the graph of the function  $y = \log x$  for  $x > 0$ .  
The curve is the graph of the function  $y = \log x$  for  $x > 0$ .



## Discussion

### A. Dielectric Measurements.

The experimental results are shown in the graphs of Figures 1 - 13. An anomalous polarizability was found only in the case of the chromium sulphate hydrate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . The sudden rise at slightly over  $160^\circ\text{K}$  corresponds with the beginning of the specific heat anomaly as found by Vasileff (7). A rounded peak in the polarizability curve occurs at about  $193^\circ\text{K}$ , corresponding with the specific heat maximum at  $195^\circ\text{K}$ . The close correspondence between the dielectric and specific heat measurements on this material, combined with the absence of an anomaly in the case of anhydrous chromium sulphate, confirms the original suspicion that the anomaly in chromium sulphate is due to a rotation associated with the water of hydration.

Since there was nothing anomalous in the dielectric behaviour of any of the salts other than the chromium sulphate hydrate, it must be concluded that the specific heat anomalies in these cases are due to something other than rotation of the dipolar water groups. The most likely explanation therefore, is that the specific heat anomalies are due to a rotation in one or more of the nitrate radicals. These are non-polar, and a change in their orientation would not affect the dielectric constant appreciably.

All the salts measured showed a rapid increase in conductivity above about  $220^\circ\text{K}$ . Above this temperature neither the conductivity nor the capacitance of the cell gave values which could be repeated during successive runs on the same sample. In any case, values of the capacitance obtained in the region where conductivity is appreciable would be considerably in doubt. Fortunately, the transition temperatures of all the materials investigated were well below this temperature, and for the low temperature conduc-



tion effects did not appear to be serious. For the hydrated salts this increase in conductivity may be associated with the water of hydration, since Dewar and Fleming (12) observed a similar increase in the conductivity of ice above 190°K.

#### B. Entropy Evidence for a Rotation Anomaly.

The excess entropy associated with the specific heat anomaly of the hydrate of chromium sulphate has been given by Vasileff and Grayson-Smith (13) as 1.41 R where R is the gas constant. This is very nearly equal to the increase in entropy which would result if two molecules of water per molecule of hydrated salt were set free at the transition temperature, and to take up either of two possible orientations. The number of new configurations available, due to this cause, would be  $2^2$  per molecule, and therefore the additional entropy would be

$$\Delta S = R \ln 4 = 1.39 R \quad (12)$$

This could be the result of a situation in which two water molecules were less tightly bound than the others to the parent molecule. Above the transition temperature the thermal energy becomes sufficient to overcome the chemical bonds for these two molecules, and they then become free to take up positions parallel or anti-parallel to the field. This is analogous to the transition of a ferromagnetic material to a paramagnetic material at its Curie point.

A quantitative check of this suggestion, based on measurements of the dielectric properties, is rather difficult to make since no adequate theory of the relationship of the dielectric constant to phase transitions is at present available. Kirkwood (14) has calculated the theoretical temperature variation of the dielectric constant of a simple dipolar material on the assumption that the dipoles become free to take up any orientation. The formula he



obtained checks very roughly with the experimental dielectric constant of hydrogen bromide in the region of its second-order transition at  $89^{\circ}\text{K}$ . It may be possible to modify his formula to apply to the present case and hence provide a quantitative check with the results of this investigation. Consideration is being given to this at the present time.

A very rough check may be made by comparison of the polarizability curve for hydrated chromium sulphate (Figure 6) with that of ice (Figure 14), calculated from the dielectric measurements of Dewar and Fleming (12). The difference between the peak polarizability of the chromium sulphate at  $193^{\circ}\text{K}$  and the extrapolation of the "normal" polarizability below  $160^{\circ}\text{K}$  to this temperature is about  $1.6 \times 10^{-23} \text{ cm}^3$ . The polarizability of ice at  $193^{\circ}\text{K}$  is approximately  $0.65 \times 10^{-23} \text{ cm}^3$ . If the polarizabilities were directly additive, this would indicate that between 2 and 3 molecules had been set free to rotate at the transition temperature. The order of this result supports the suggestion that two water molecules are set free during the transition.



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